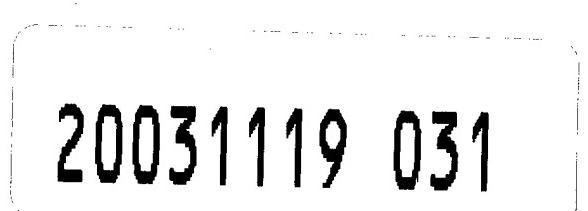


# REPORT DOCUMENTATION PAGE

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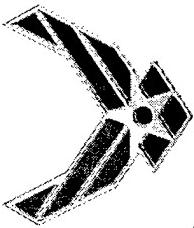
# Design, Synthesis and Characterization of New Ionic Liquids

Greg Drake and Tom Hawkins  
AFRL/PRSP  
Air Force Research Laboratory  
Edwards AFB, CA 93524



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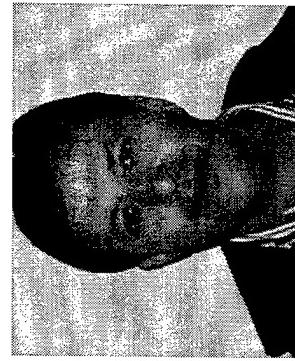
# Ionic Liquids



## Those involved in this work



Ms. Kerri Tollison  
Synthesis and  
Characterization



Greg Kaplan  
Synthesis and  
Characterization



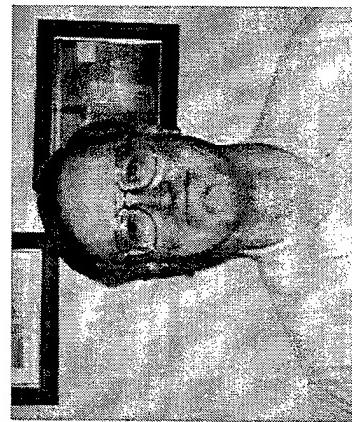
Jerry Boatz  
Theoretical  
Calculations



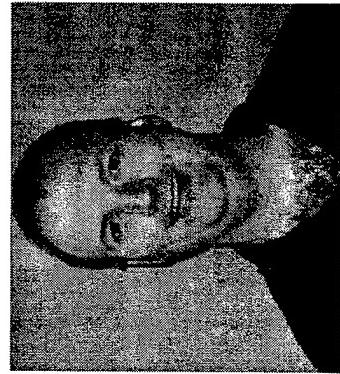
Leslie Hall  
Synthesis &  
X-ray work



Ashwani Viji  
X-ray  
crystallography



Tommy Hawkins  
6.2 Propellant  
Development



Jeff Mills  
Theoretical  
Calculations

Greg Drake  
6.1 Research  
Synthesis

2

# Ionic Liquids

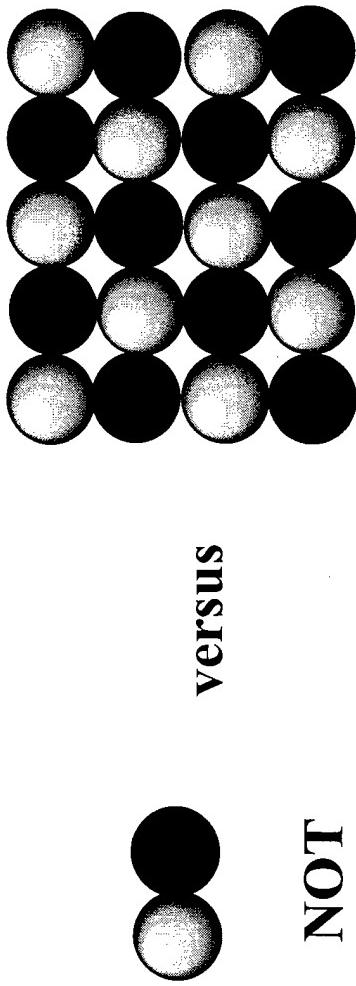
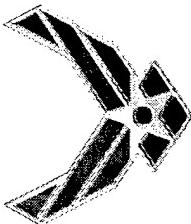


Table salt  $\text{Na}^+\text{Cl}^-$  m.p. =  $804^\circ\text{C}$  Very high  
Cryolite  $\text{Na}_3\text{AlF}_6$  m.p. nearly  $1000^\circ\text{C}$  (Hall Process for Al production)  
Eutectic of  $\text{Li}^+\text{Cl}^-$  and  $\text{K}^+\text{Cl}^-$  m.p.  $355^\circ\text{C}$

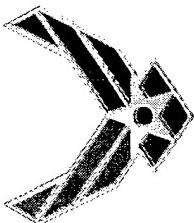
Molten salts are very hot!

Not commercially viable

Corrosion and energy issues

Giant lattice of miniature magnets stuck together

# Ionic Liquids



What are Ionic Liquids?

A class of salts consisting of cation/anion pair that has a very low melting point.

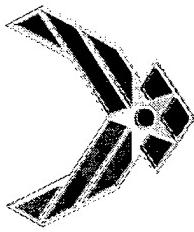
Definition of an ionic liquid is open to some debate amongst researchers in the area, but most in the area use one of two.

(1) An ionic compound that melts below 100 °C (b.p. of H<sub>2</sub>O). J. Wilkes, P. Wasserscheid, K. Seddon.

(2) An ionic compound that has a melting point at or below ambient temperatures. These are often called RTILs (Room Temperature Ionic Liquids) T. Welton, R. Rogers.

But many of the salts fit both definitions and (2) is really a more specific class of (1).

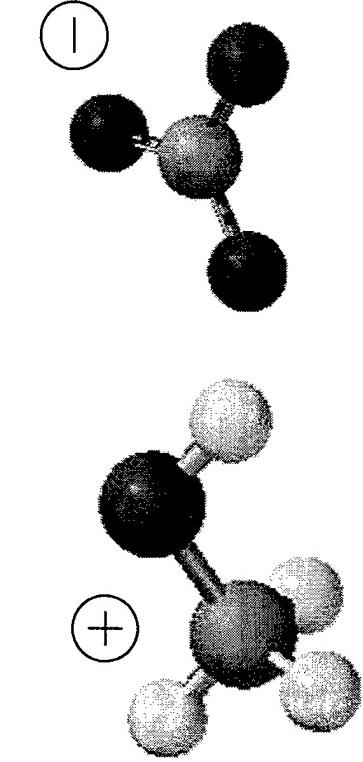
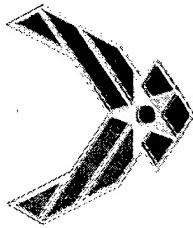
# Ionic Liquids



## Important factors affecting the physical properties of ionic liquids

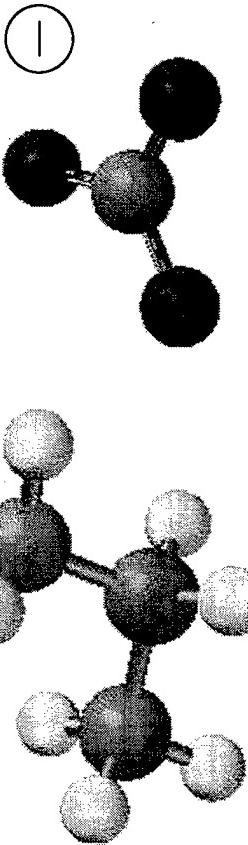
1. Asymmetry of cation as well as anion
2. Packing efficiency
3. Charge delocalization in cationic/anionic species
4. “Sheer size” differentials

# Ionic Liquids



(+)

(+)



(-)

## Hydroxylammonium nitrate (HAN)

$[\text{NH}_3\text{OH}^+][\text{NO}_3^-]$  m.p. 39-40 °C

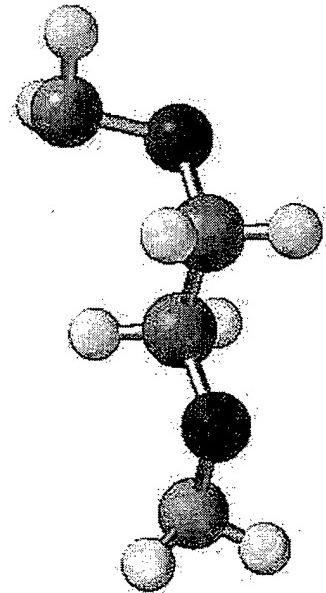
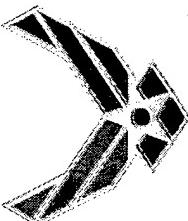
## Ethylammonium nitrate $[\text{CH}_3\text{CH}_2\text{NH}_3^+][\text{NO}_3^-]$ m.p. 12 °C

Serious issues...

- can be treacherous
- acidic
- very hygroscopic

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# Ionic Liquids

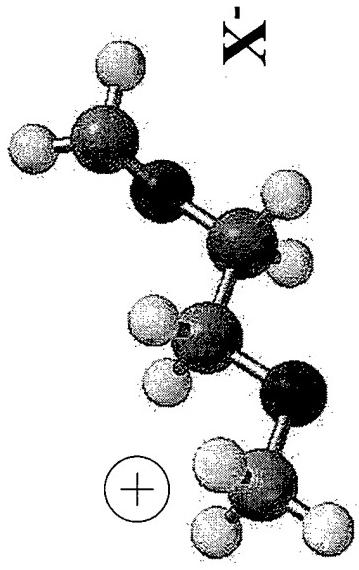


H-X



## 1,2-bis(oxyamine)ethane

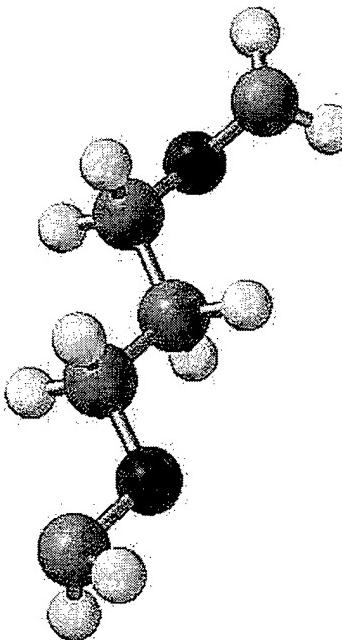
Dixon, D. W.; Weiss, R. H. *J. Org. Chem.* 1984, 49, 4487



X-

## 1,2-bis(oxyamine)ethane mono salts

X<sup>-</sup> = NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, C(NO<sub>2</sub>)<sub>3</sub><sup>-</sup>, N(NO<sub>2</sub>)<sub>2</sub><sup>-</sup>



H-X

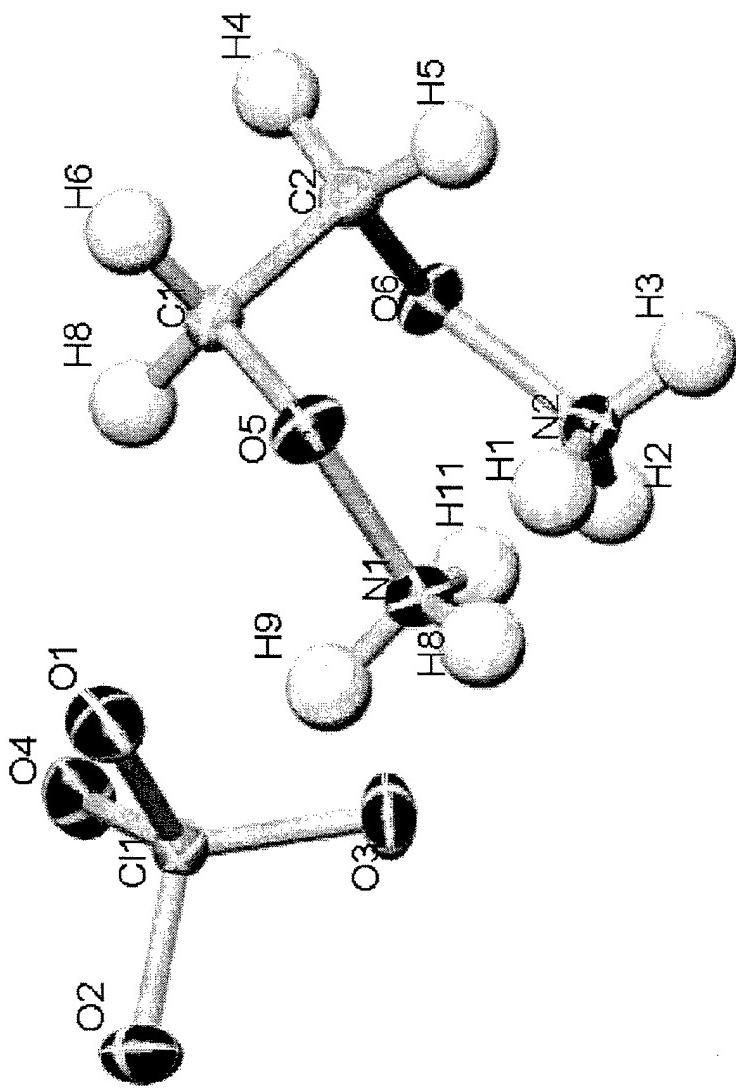
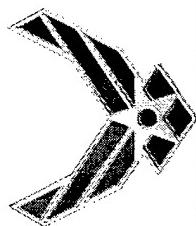


1,3-bis(oxyamine)propane very stable, watery liquid  
b.p. = 65-70 °C @ 0.3 torr; f.p. = glasses at -40 °C

X<sup>-</sup> = NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, C(NO<sub>2</sub>)<sub>3</sub><sup>-</sup>, N(NO<sub>2</sub>)<sub>2</sub><sup>-</sup>

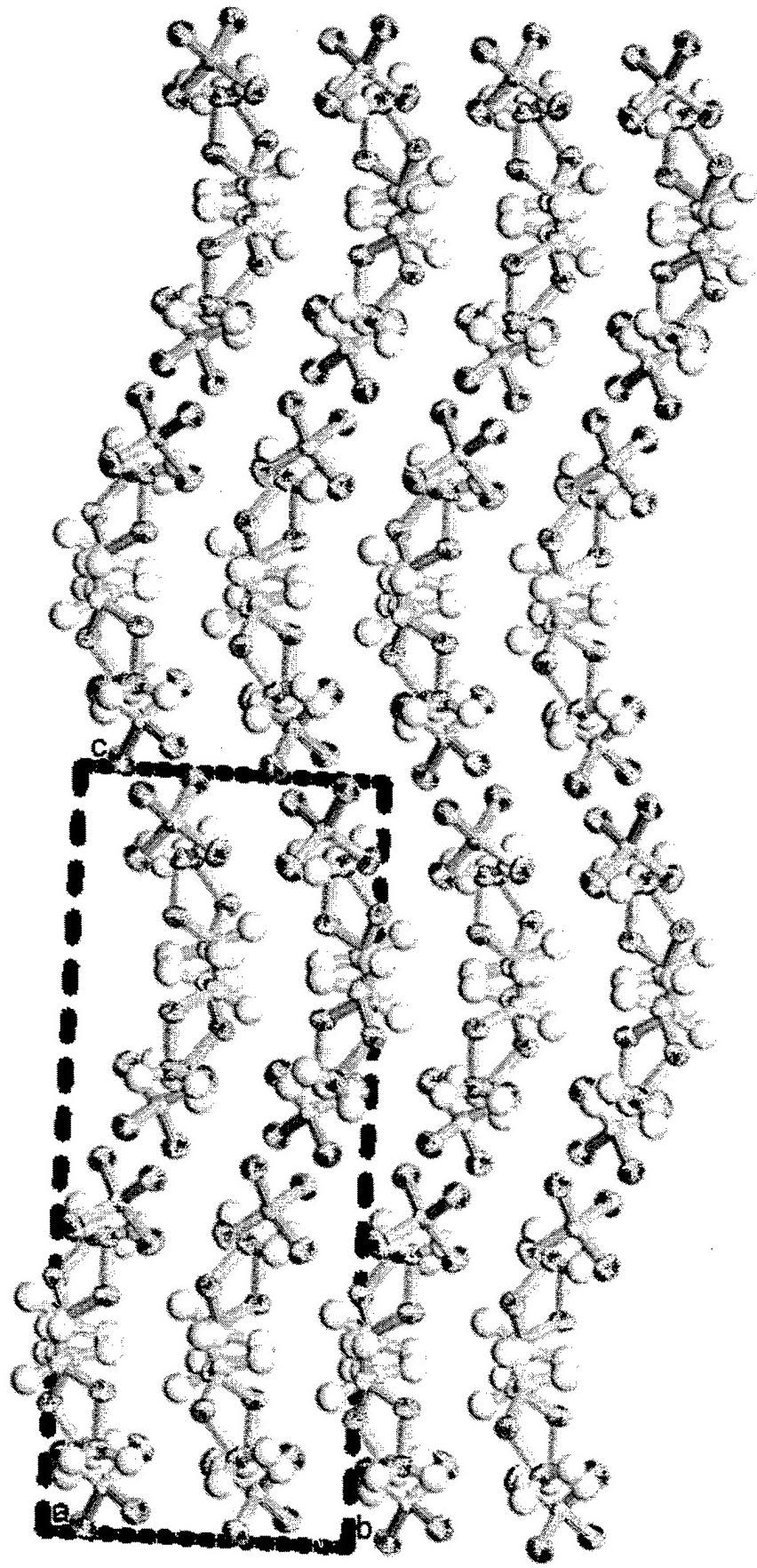
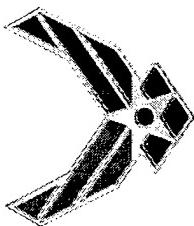
Bisoxamines are stable as neutrals but protonated versions are not (extremely friction and impact sensitive!) Direct contrast with simple mono oxyamines.

# Ionic Liquids



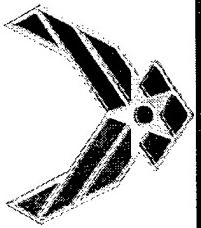
Single crystal X-ray structure of ethylene bisoxazoline monoperchlorate. Material has unusual amount of hydrogen bonding present ( $\rho = 1.83 \text{ g/cm}^3$ !!!), but that doesn't explain its extreme sensitivity to impact and friction.

# Ionic Liquids

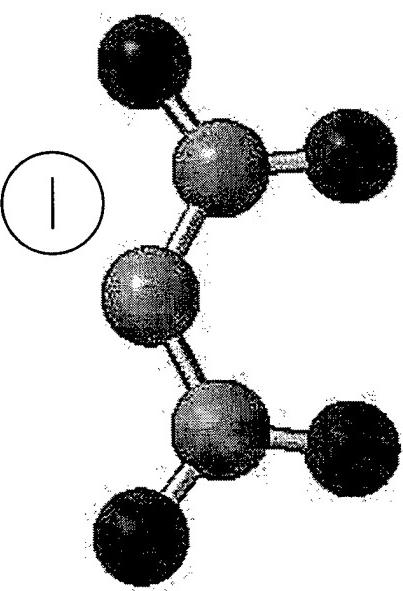


Extended lattice of ethylene bisoxamide monoperchlorate.

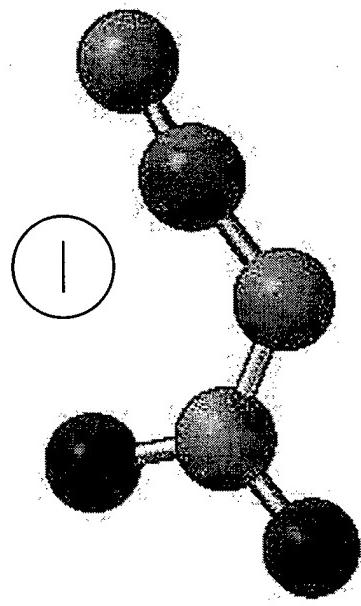
# Ionic Liquids



Since its western discovery in the late 1980's, by Jeff Bottaro, the dinitramide anion,  $\text{N}(\text{NO}_2)_2^-$  has received tremendous attention as a potential new oxidizing anion for energetic materials. A closely related anion, the nitrocyanamide anion,  $\text{N}(\text{NO}_2)(\text{CN})^-$ , was discovered in the early 1950's by McKay, and shortly thereafter, Harris investigated many heavy metal salts, as possible replacement initiators. However, it has been virtually ignored since that time.



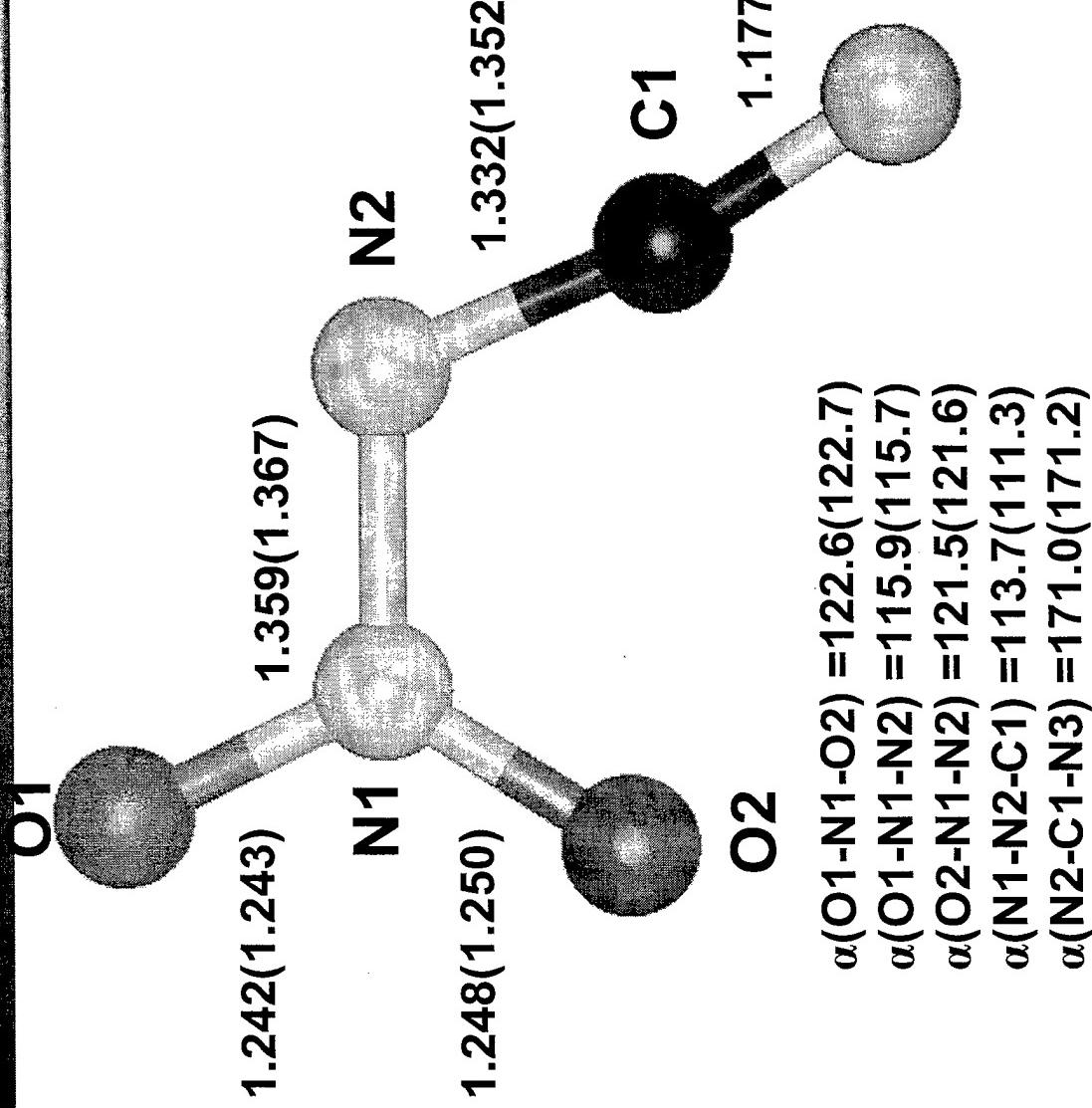
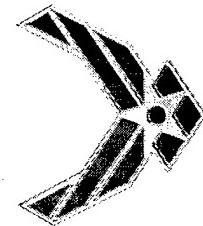
$\text{N}(\text{NO}_2)_2^-$  (dinitramide)



$\text{N}(\text{NO}_2)(\text{CN})^-$  (nitrocyanamide)

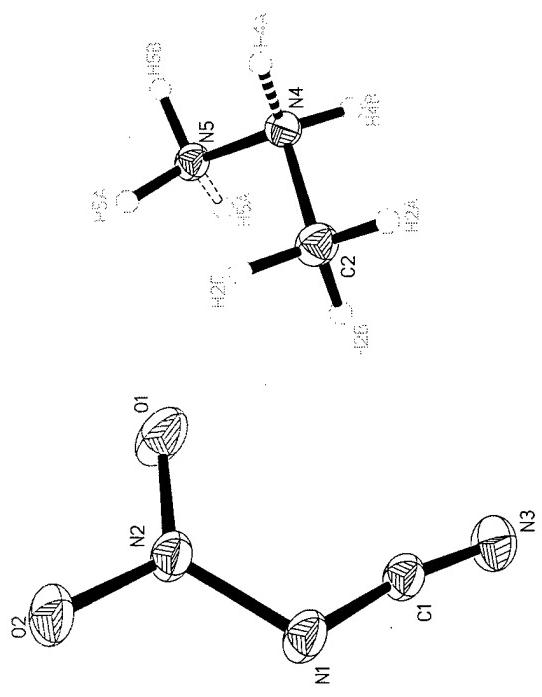
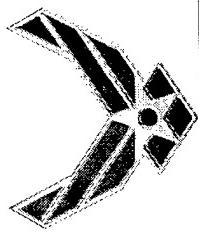
Bottaro, J. L. ; Penwell, P. E. ; Schmitt, R. J. Synth. Commun., 1991, 21, 945  
McKay, A. F. ; Ott, W. L. ; Taylor, G. W. ; Buchanan, M. N. ; Crooker, J. F. Can. J. Chem., 1951, 28, 683 ; Harris, S. J. Amer. Chem. Soc., 1958, 80, 2302.

# Ionic Liquids

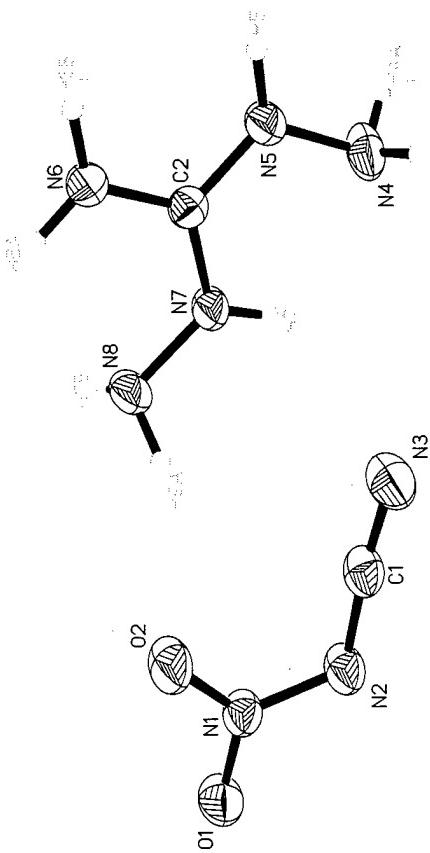


$$\begin{aligned}\alpha(\text{O}_1\text{-N}_1\text{-O}_2) &= 122.6(122.7) \\ \alpha(\text{O}_1\text{-N}_1\text{-N}_2) &= 115.9(115.7) \\ \alpha(\text{O}_2\text{-N}_1\text{-N}_2) &= 121.5(121.6) \\ \alpha(\text{N}_1\text{-N}_2\text{-C}_1) &= 113.7(111.3) \\ \alpha(\text{N}_2\text{-C}_1\text{-N}_3) &= 171.0(171.2)\end{aligned}$$

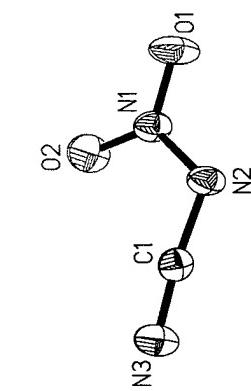
# Ionic Liquids



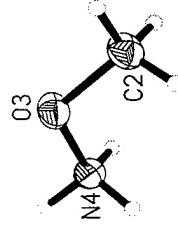
Monomethylhydrazinium nitrocyanamide



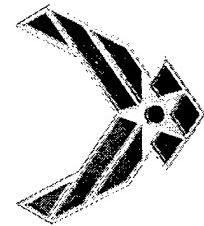
Diaminoguanidinium nitrocyanamide



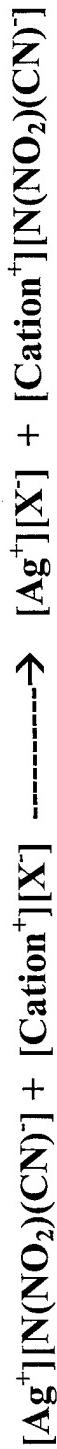
Methoxyammonium nitrocyanamide



# Ionic Liquids



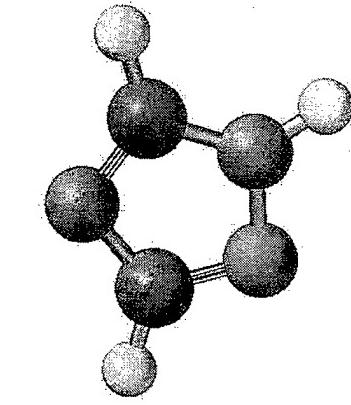
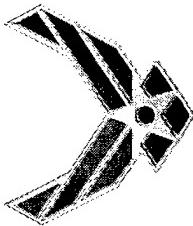
- The syntheses of several nitrocyanamide salts were accomplished through the metathesis reactions of the appropriate halide salt with silver nitrocyanamide as Harris reported in 1958.



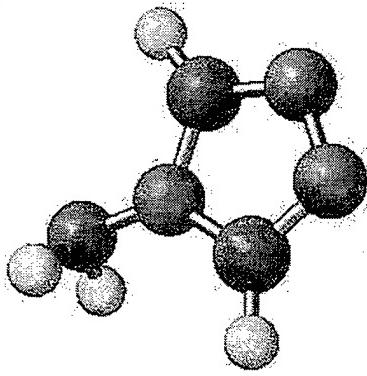
<u>Compound</u>	$\Delta H_f(\text{est})$ Kcal/mole	M.P. $^{\circ}\text{C}$	Density g/cm <sup>3</sup> (meas.)	Impact kg-cm (5neg.)	Friction (Newtons) (5 neg.)	TGA % Loss/Day @ 75° C
Hydrazinium nitrocyanamide	+14	109	1.53	10	76	>1
Guanidinium nitrocyanamide	-13	95	1.39	>200	141	0.68
Methoxyammonium nitrocyanamide	-5	99	1.51	18	149	>20
Monomethylhydrazinium nitrocyanamide	+4	57	1.44	>200	>371	1.9
Aminoguanidinium nitrocyanamide	0	94	1.50	>200	>371	0.9
Diaminoguanidinium nitrocyanamide	+10	108	1.52	>200	>371	1.6

$[\text{NH}_3\text{OH}^+]$  and  $[\text{HO}-\text{CH}_2\text{CH}_2-\text{NH}_3^+]$  salts were made, but were not stable at ambient temperatures!

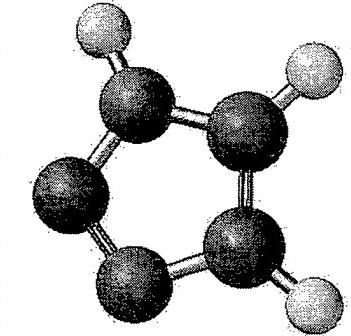
# Ionic Liquids



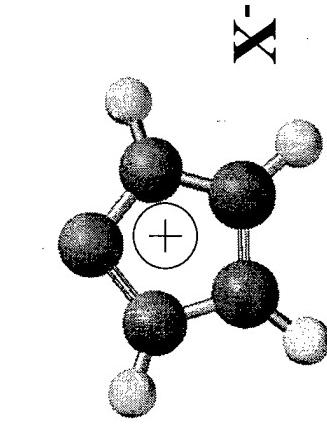
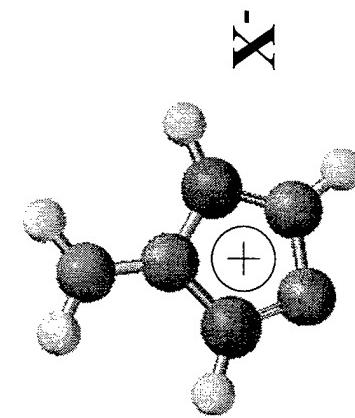
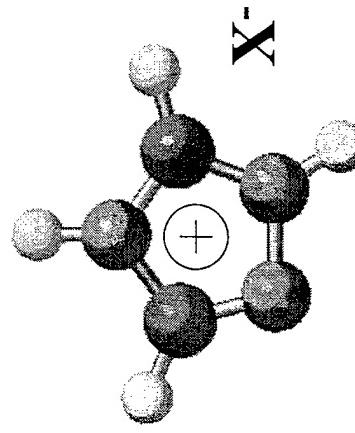
1-H-1,2,4-triazole



4-amino-1,2,4-triazole



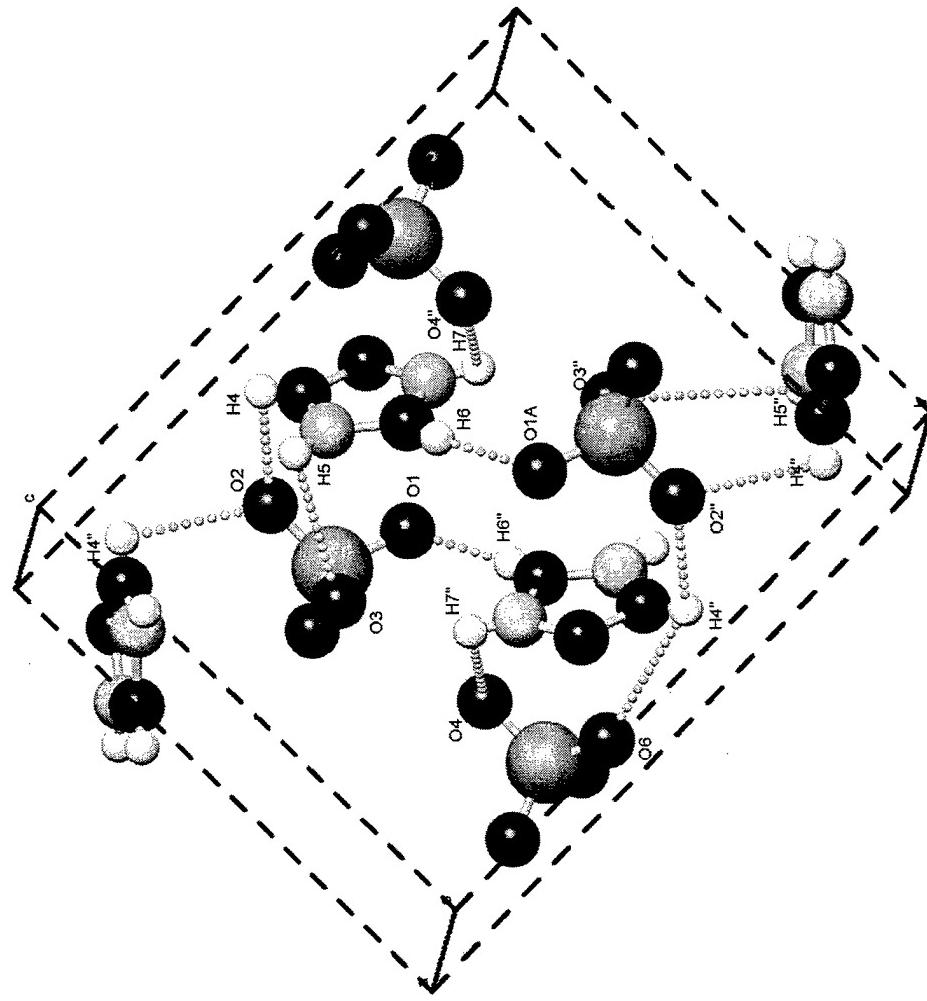
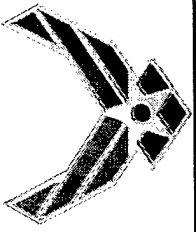
1-H-1,2,3-triazole



$$X^- = \text{NO}_3^-, \text{ClO}_4^-, \text{N}(\text{NO}_2)_2^-$$

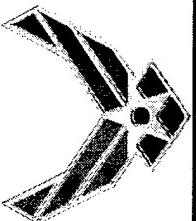
Drake, G.W. ; Hawkins, T. ; Brand, A. ; McKay, A. ; Ismail, I. ; Hall, L. ; Vij, A. Prop. Explos. Pyrotech. 2003, 12, 1.

# Ionic Liquids

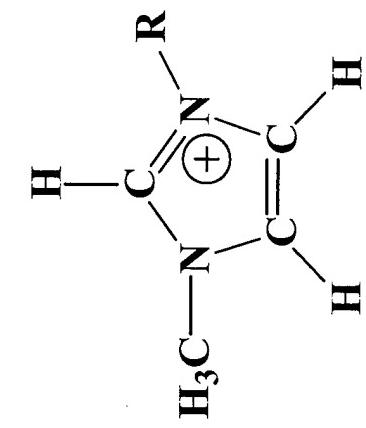


X-ray single crystal diffraction study of 1,2,4-triazolium perchlorate  $\rho = 1.96 \text{ g/cm}^3$   
It is felt that this is probably the top of the hill density wise for simple heterocycle salts.

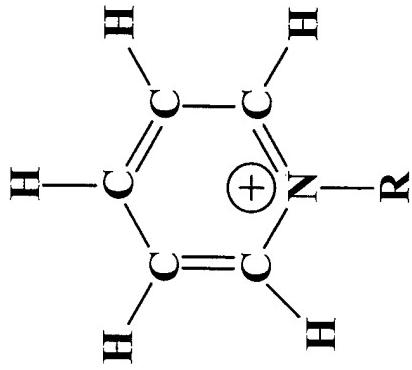
# Ionic Liquids



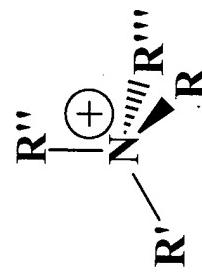
## Some major shapes for organic based cations



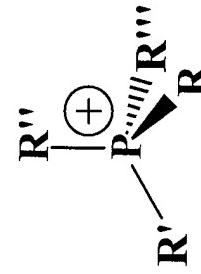
## 1-methyl-3-alkyl-imidazolium



## 1-alkylpyridinium

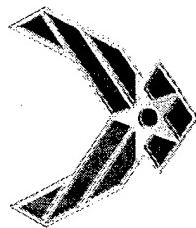


## Tetraalkylammonium

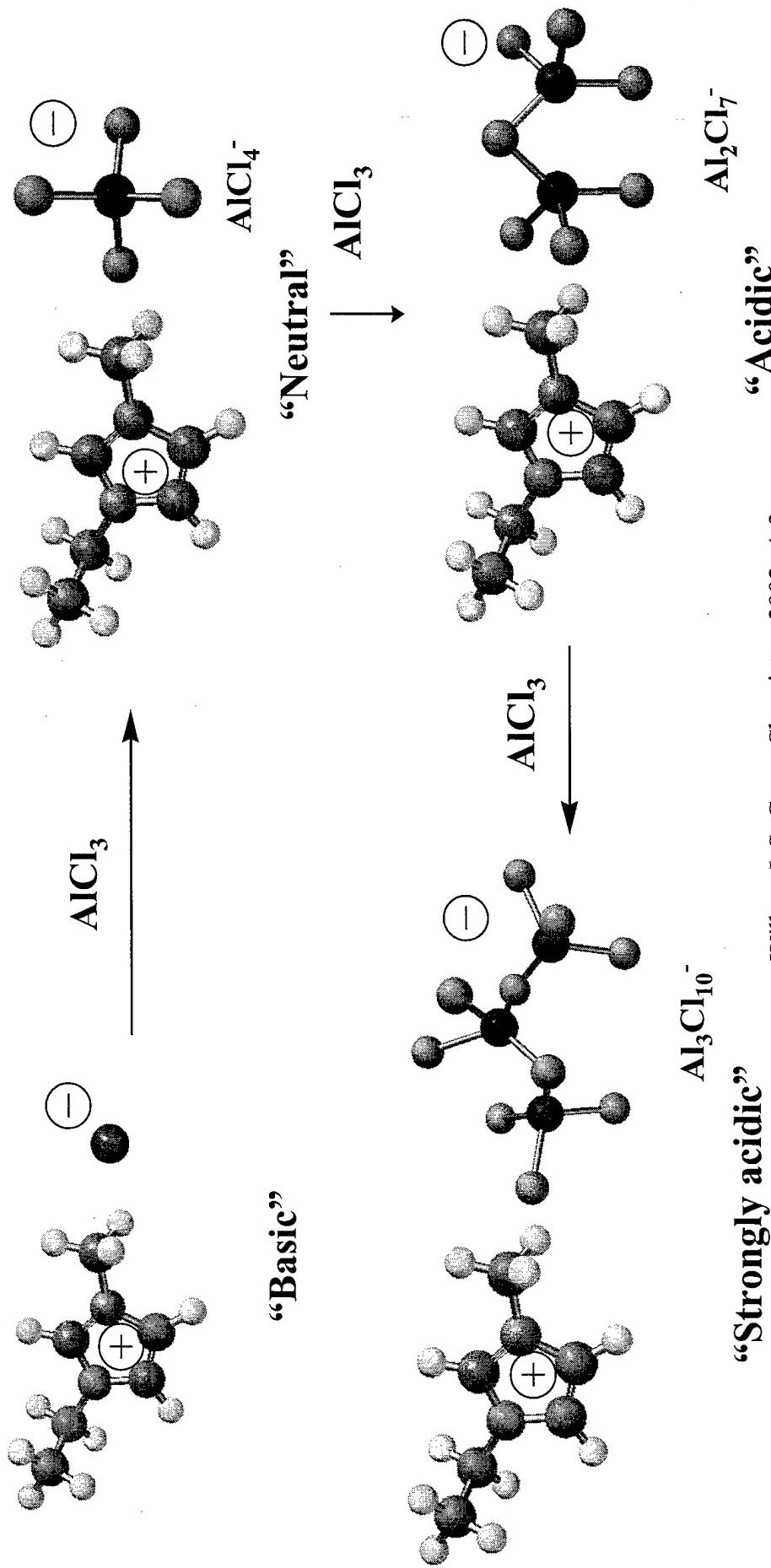


## Tetraalkylphosphonium

# Ionic Liquids

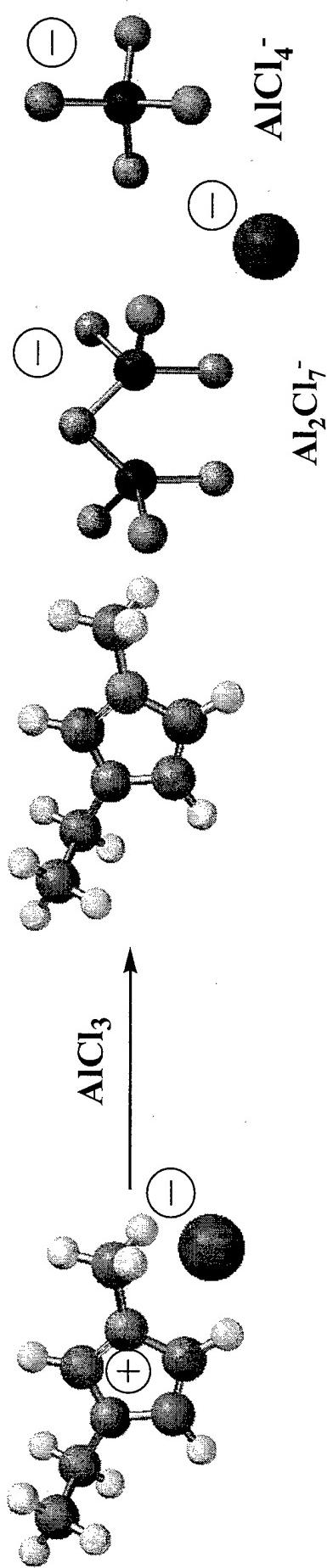
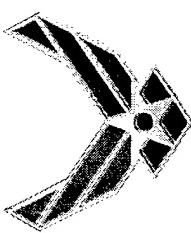


Significant efforts spent on 1-ethyl-3-methyl-imidazolium based systems and aluminum trichloride systems. More complex than originally thought as  $\text{AlCl}_3$  and  $\text{Cl}^-$  have an equilibrium based on their respective concentrations.

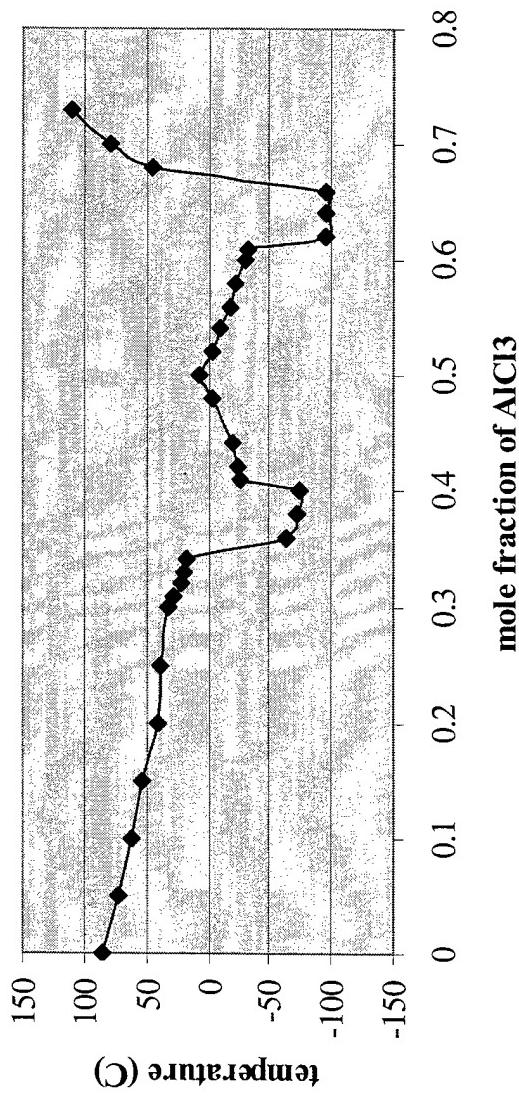


Wilkes, J. S. Green Chemistry 2002, 4, 3.

# Ionic Liquids

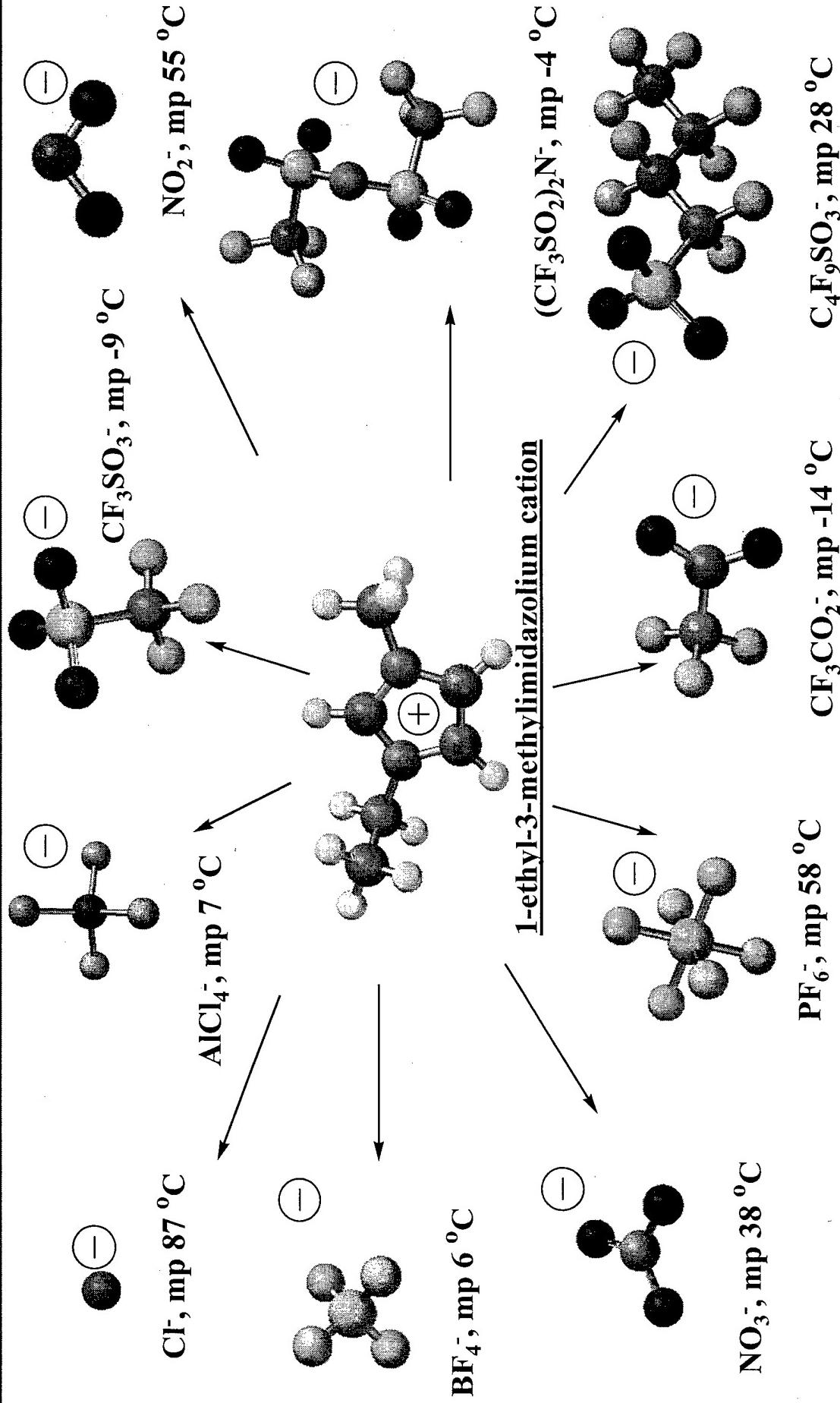
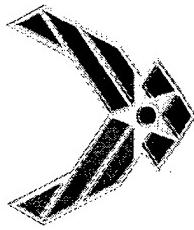


Melting point of MeEtImCl and AlCl<sub>3</sub> mixtures



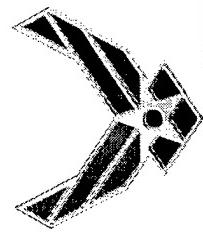
Fannin, A. ; Floreani, D. ; King, L. ; Landers, J. ; Pierson, B. ; Stretch, D. ; Vaughn, R. ; Wilkes, J. ; Williams, J. J. Phys. Chem. 1984, 88, 2614.

# Ionic Liquids

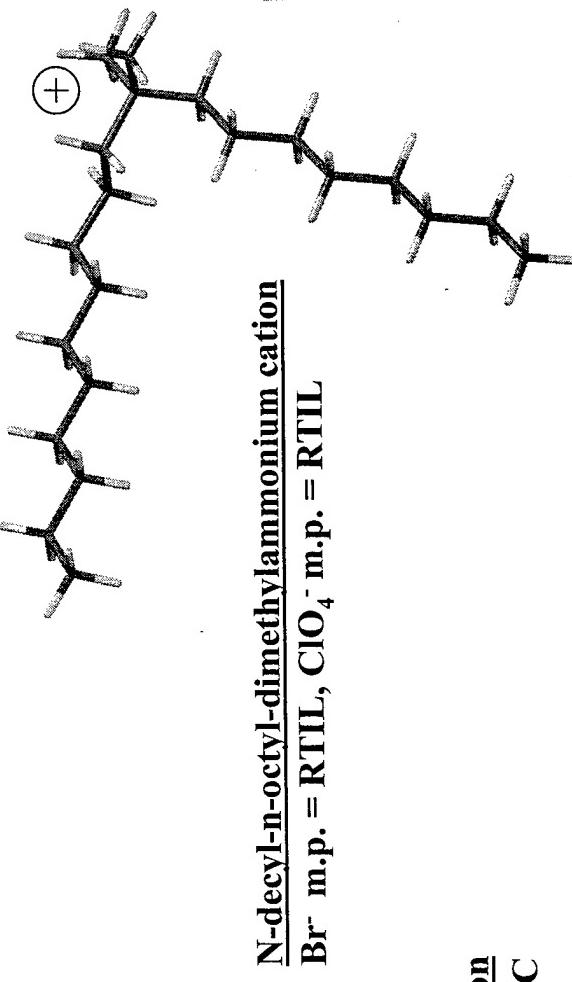
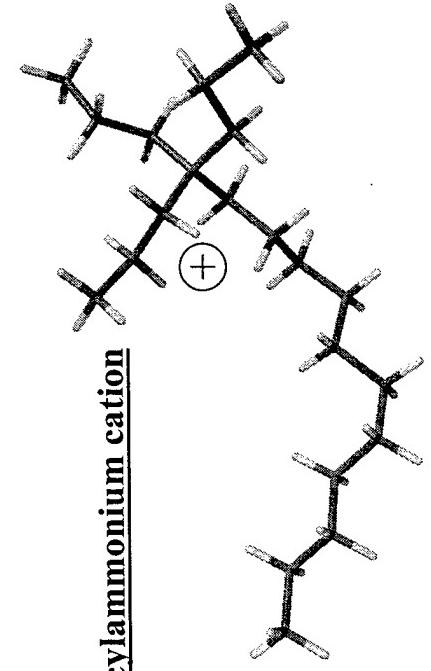
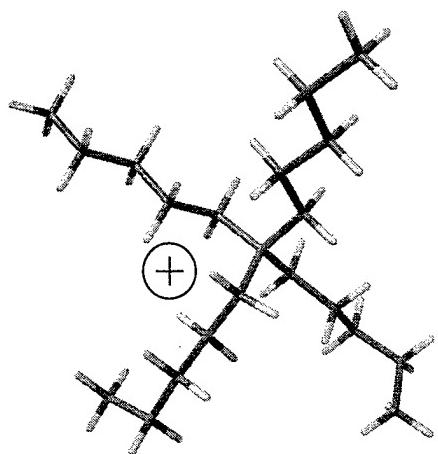


Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed. Engl.* 2000, 39, 3772. Wasserscheid, P., Welton, T. (eds.) *Ionic Liquids in Synthesis* Wiley-VCH, FRG, 2003.  
 .Seddon, K.R.; Holbrey, J. D. *Clean Products and Processes* 1999, 1, 223. Rogers, R.; Seddon, K. (eds.) *Ionic Liquids A.C.S. Symp. Ser.* 818 2002 A.C.S Publ. Co.

# Ionic Liquids

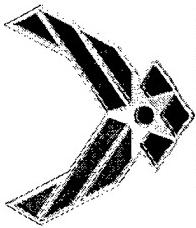


Substituted ammonium salts  $R_4N^+X^-$  Variations in melting point based on cation structure.



Gordon, J. E. ; SubbaRao, G. N. J. Amer. Chem. Soc. 1978, 100, 7445.

# Ionic Liquids

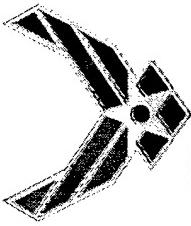


Substituted ammonium salts  $[R_4N^+][X^-]$  Recently work has been done by using more desirable anions.

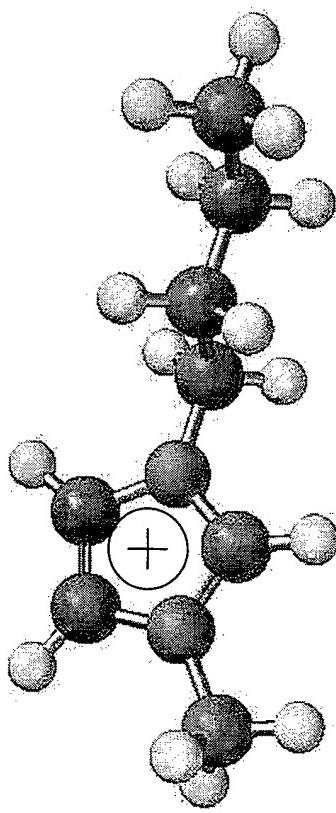
<u>Substituted Ammonium Salt</u>	<u>M.P. (°C)</u>	<u>Density (g/cm³)</u>	<u>Viscosity (cp)</u>	<u><math>\Delta</math> (<math>\Omega^{-1}</math> cm²/mole)</u>
$[(n-C_6H_{13})(CH_3)_3N^+][N(SO_2CF_3)_2]$	-74 (g)	1.33	153	1.4
$[(n-C_7H_{15})(CH_3)_3N^+][N(SO_2CF_3)_2]$	-73 (g)	1.28	153	1.4
$[(n-C_8H_{17})(CH_3)_3N^+][N(SO_2CF_3)_2]$	-73 (g)	1.27	181	1.3
$[(n-C_6H_{13})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2]$	20	1.27	167	2.5
$[(n-C_7H_{15})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2]$	-79	1.26	75	1.9
$[(n-C_8H_{17})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2]$	-74	1.25	202	1.3
$[(n-C_6H_{13})(n-C_4H_9)_3N^+][N(SO_2CF_3)_2]$	26	1.15	595	0.8
$[(n-C_7H_{15})(n-C_4H_9)_3N^+][N(SO_2CF_3)_2]$	-67	1.17	606	0.8
$[(n-C_8H_{17})(n-C_4H_9)_3N^+][N(SO_2CF_3)_2]$	-63	1.12	574	0.7
$[(n-C_7H_{15})(Et)_3(ipr)_2N^+][N(SO_2CF_3)_2]$	-82	1.27	362	1.2
$[(n-C_8H_{17})(n-C_4H_9)_3N^+][OSO_2CF_3]$	-57	1.02	2030	0.07

- most have very low glass points
- densities decrease as expected
- viscosity increases dramatically with increasing alkyl length
- conductivity decreases with cation size (mobility issue)

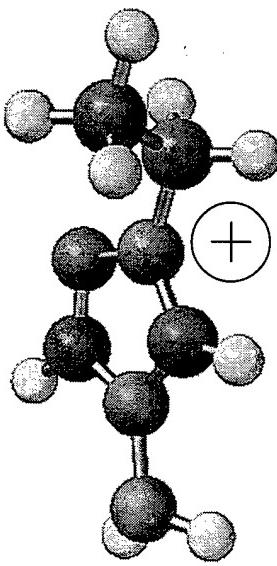
# Ionic Liquids



Most ionic liquids are based upon imidazolium rings and “heavy” or “dead” anions. We felt that we could use the shape of the cation and the poor fit idea to make much more energetic salts in a simple manner.



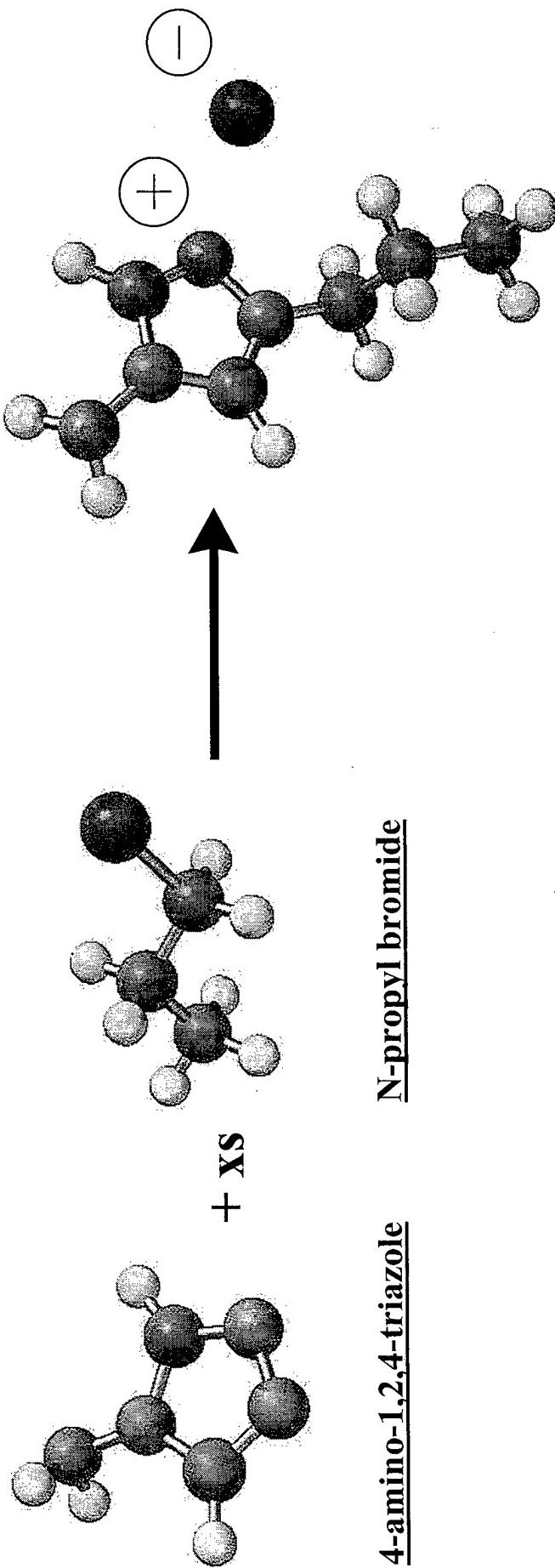
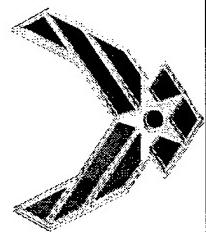
1-n-butyl-3-methyl imidazolium cation



1-ethyl-4-amino-1,2,4-triazolium cation

These new ionic liquids have similar shapes and physical properties,  
BUT higher  $\Delta H_p$ , higher densities, and better oxygen balances.

# Ionic Liquids

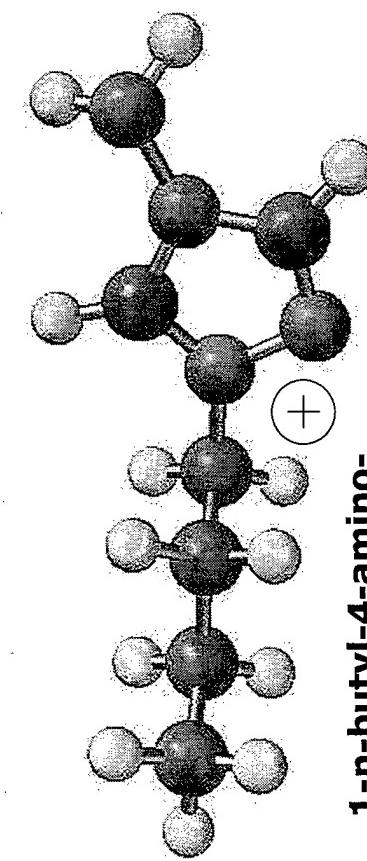
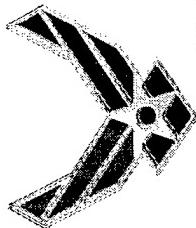


Synthesis is from commercial materials

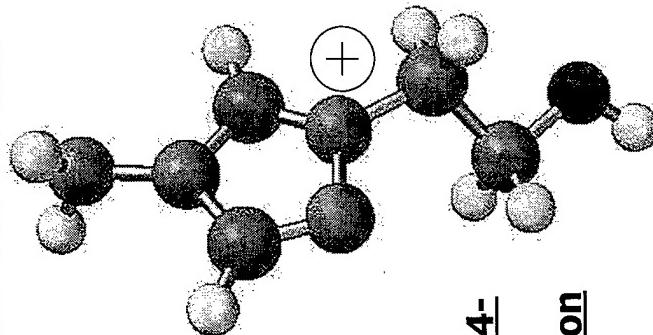
High yield simple isolation has been known  
in literature for quite some time.  
  
*1-n-propyl-4-amino-*  
**1,2,4-triazolium bromide**  
(yield >95% very pure)

Scriven; Keay; Goe; Astleford J. Org. Chem. 1989, 54, 731.

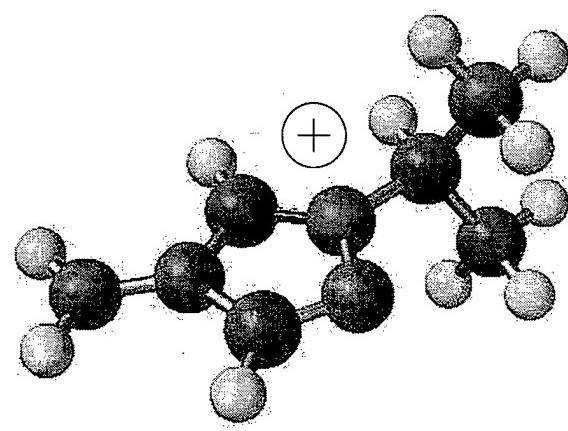
# Ionic Liquids



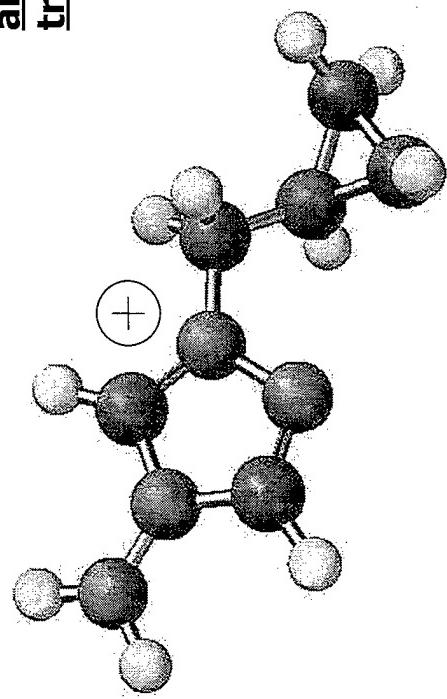
1-n-butyl-4-amino-  
1,2,4-triazolium cation



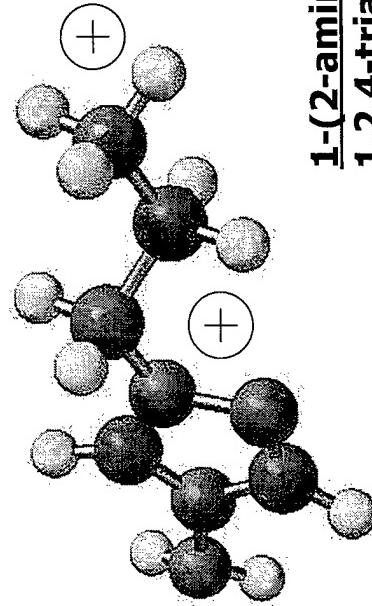
1-(2-ethanol)-4-  
amino-1,2,4-  
triazolium cation



1-isopropyl-4-amino-  
1,2,4-triazolium cation

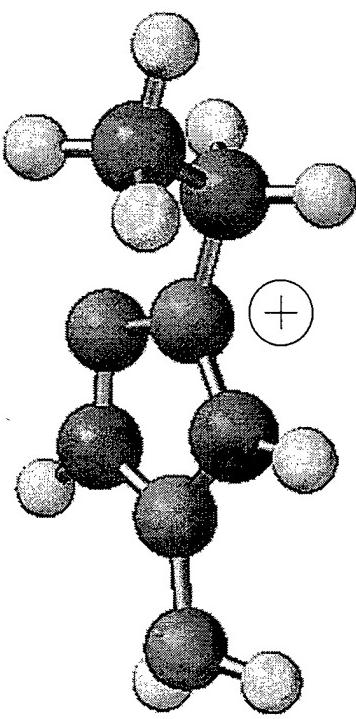
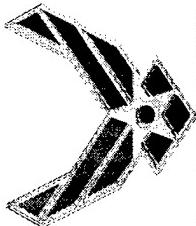


1-methylcyclopropyl-4-amino-  
1,2,4-triazolium cation

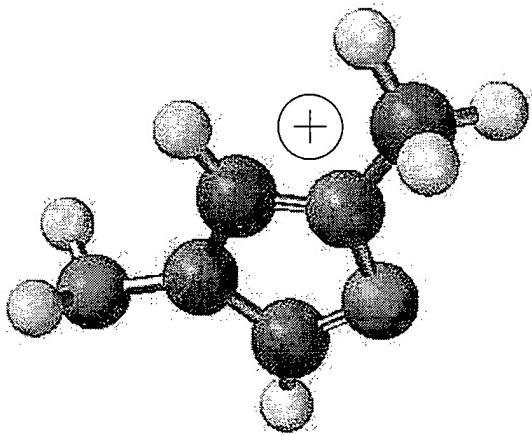


1-(2-aminoethyl)-4-amino-  
1,2,4-triazolium cation

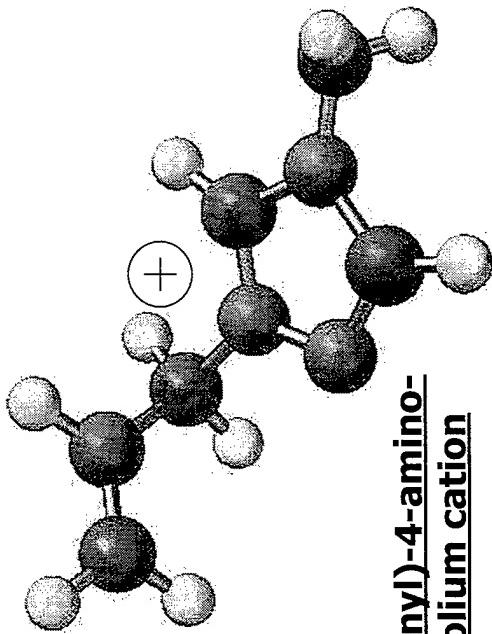
# Ionic Liquids



1-ethyl-4-amino-  
1,2,4-triazolium cation



1-methyl-4-amino-  
1,2,4-triazolium cation

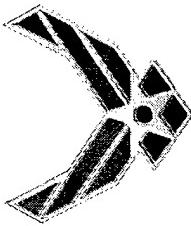


1-(2-propenyl)-4-amino-  
1,2,4-triazolium cation



1-n-propyl-4-amino-  
1,2,4-triazolium cation

# Ionic Liquids

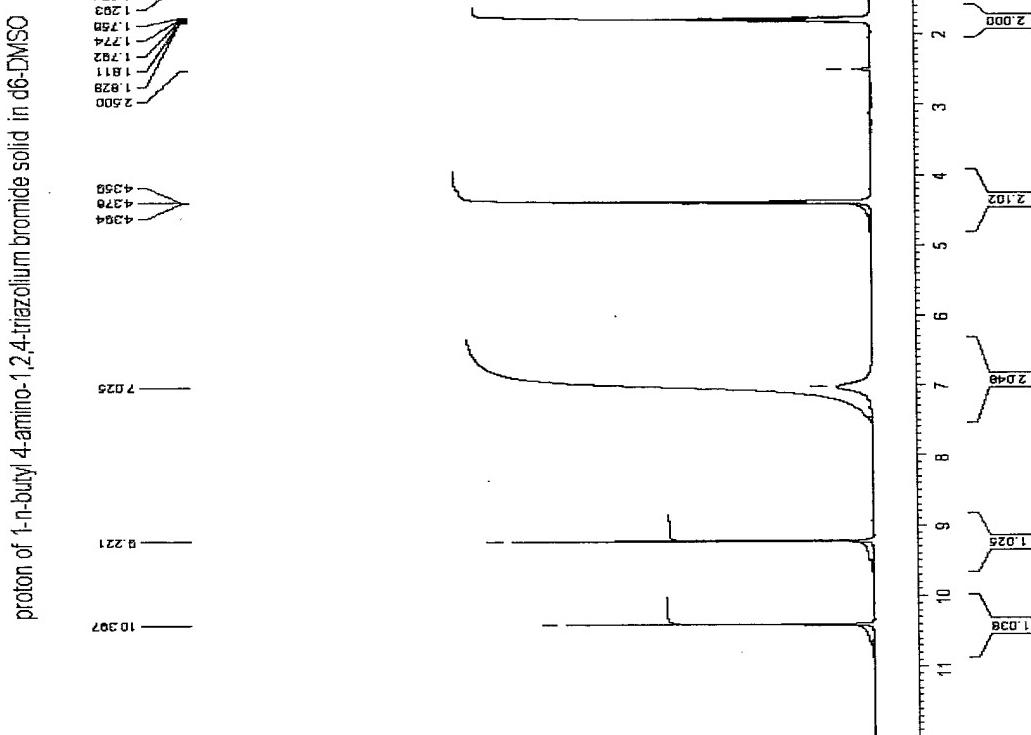
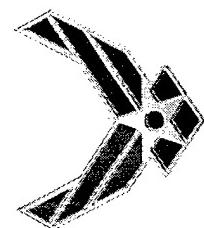


Physical properties of 1-n-alkyl substituted-4-amino-1,2,4-triazolium bromides.

- increasing melting points with increasing molecular weights,
- decomposition onsets that are relatively low
- densities decrease with increasing alkyl chain length.

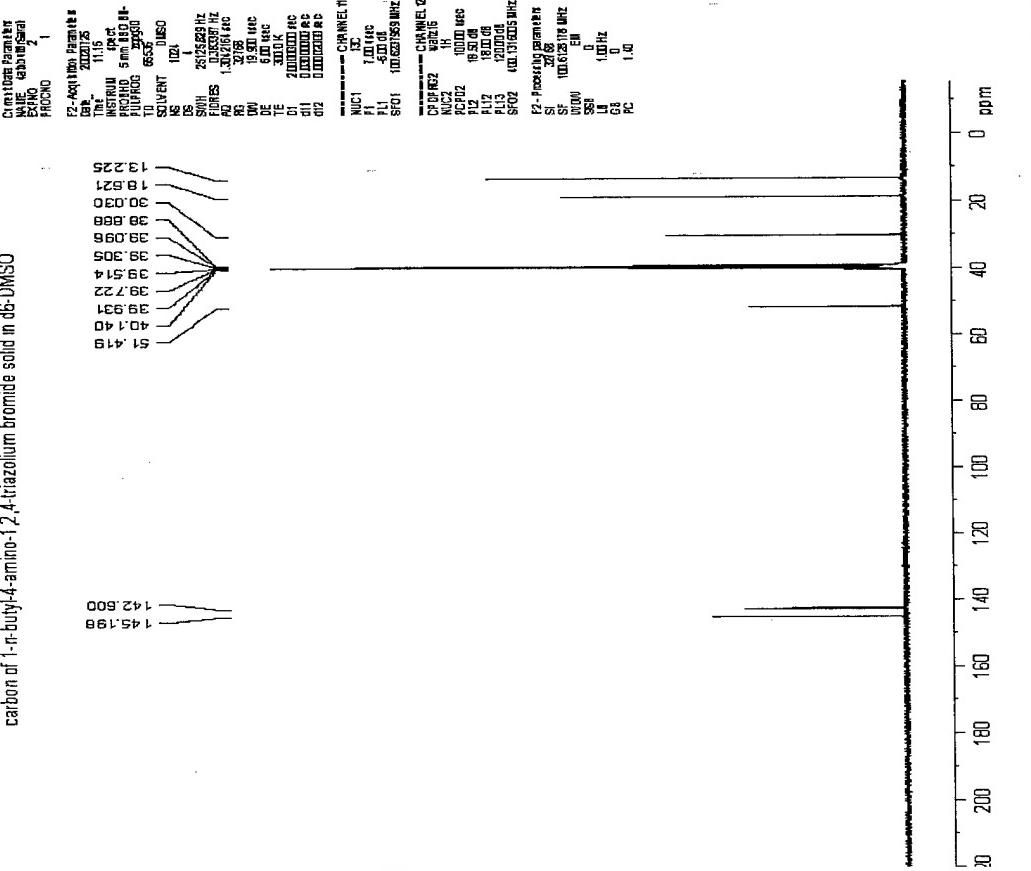
Substituted 4AT salts	m.p. (°C)	dec. onset (°C)	density (g/cm <sup>3</sup> )
1-ethyl	63°	110	1.69
1-n-propyl	60°	120	1.56
1-isopropyl	90°	110	1.60
1-butyl	48°	130	1.46
1-n-pentyl	54°	130	1.37
1-n-hexyl	76°	120	1.34
1-n-heptyl	94°	120	1.30
1-n-octyl	80°	135	1.27
1-n-nonyl	81°	140	1.26
1-n-decyl	90°	135	1.23

## Ionic Liquids



proton of 1-n-butyl 4-amino-1,2,4-triazolium bromide solid in d6-DMSO

Current Data Parameters  
NAME: 4thInfluenza  
EXPNO:



Carbon of 1-*n*-butyl-4-amino-1,2,4-triazolium bromide solid in de-DMSO

carbon of 1-n-butyl-4-amino-12,4-triazolium bromide solid in D<sub>2</sub>-DMSO

**Current Data Parameters**

NAME	4AminobutGrah
ENDO	1
PICNO	1

**F1 - Acquisition Parameters**

Date	20100726
Time	10:46
INSTRUM	Spect
PROBOD	5 mm BBO BB
PULPROG	65536Q
TD	65536
SOVTIME	1.000
SOV	32
DS	2
SWH	8278.140 Hz
FOIDRES	0.12014 Hz
SWFID	3.0564643 sec
RG	65.8
TDZ	0.0100 usec
TE	6.000 usec
DW	1.0000 sec
D1	1.000000 sec

**CHANNEL 1**

NUC1	<sup>1</sup> H
PL1	720 usec
PL1	8100 dB
SF01	400.132491 MHz

**CHANNEL 2**

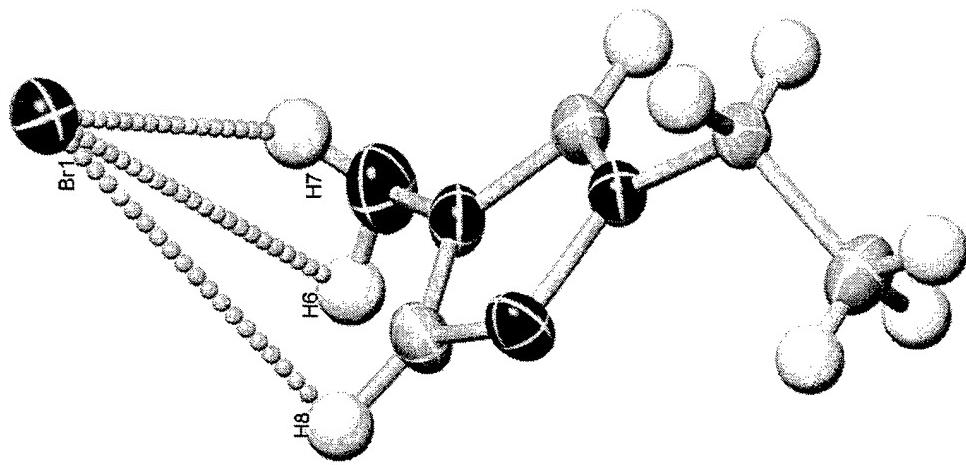
NUC1	<sup>13</sup> C
PL1	720 usec
PL1	8100 dB
SF01	400.130030 MHz
SI	32768
PC	1.00

**F2 - Processing parameters**

SWH	11.5 Hz
TD	2048
TE	65.5 sec
DW	10.0 sec
SWFID	0.000000 sec
RG	0.000000 sec
DW1	10.0 sec
SWFID1	0.000000 sec
TD1	2048
TE1	65.5 sec
DW2	10.0 sec
SWFID2	0.000000 sec
TD2	2048
TE2	65.5 sec
DW3	10.0 sec
SWFID3	0.000000 sec
TD3	2048
TE3	65.5 sec
DW4	10.0 sec
SWFID4	0.000000 sec
TD4	2048
TE4	65.5 sec
DW5	10.0 sec
SWFID5	0.000000 sec
TD5	2048
TE5	65.5 sec
DW6	10.0 sec
SWFID6	0.000000 sec
TD6	2048
TE6	65.5 sec
DW7	10.0 sec
SWFID7	0.000000 sec
TD7	2048
TE7	65.5 sec
DW8	10.0 sec
SWFID8	0.000000 sec
TD8	2048
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DW9	10.0 sec
SWFID9	0.000000 sec
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SWFID12	0.000000 sec
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TE12	65.5 sec
DW13	10.0 sec
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DW24	10.0 sec
SWFID24	0.000000 sec
TD24	2048
TE24	65.5 sec
DW25	10.0 sec
SWFID25	0.000000 sec
TD25	2048
TE25	65.5 sec

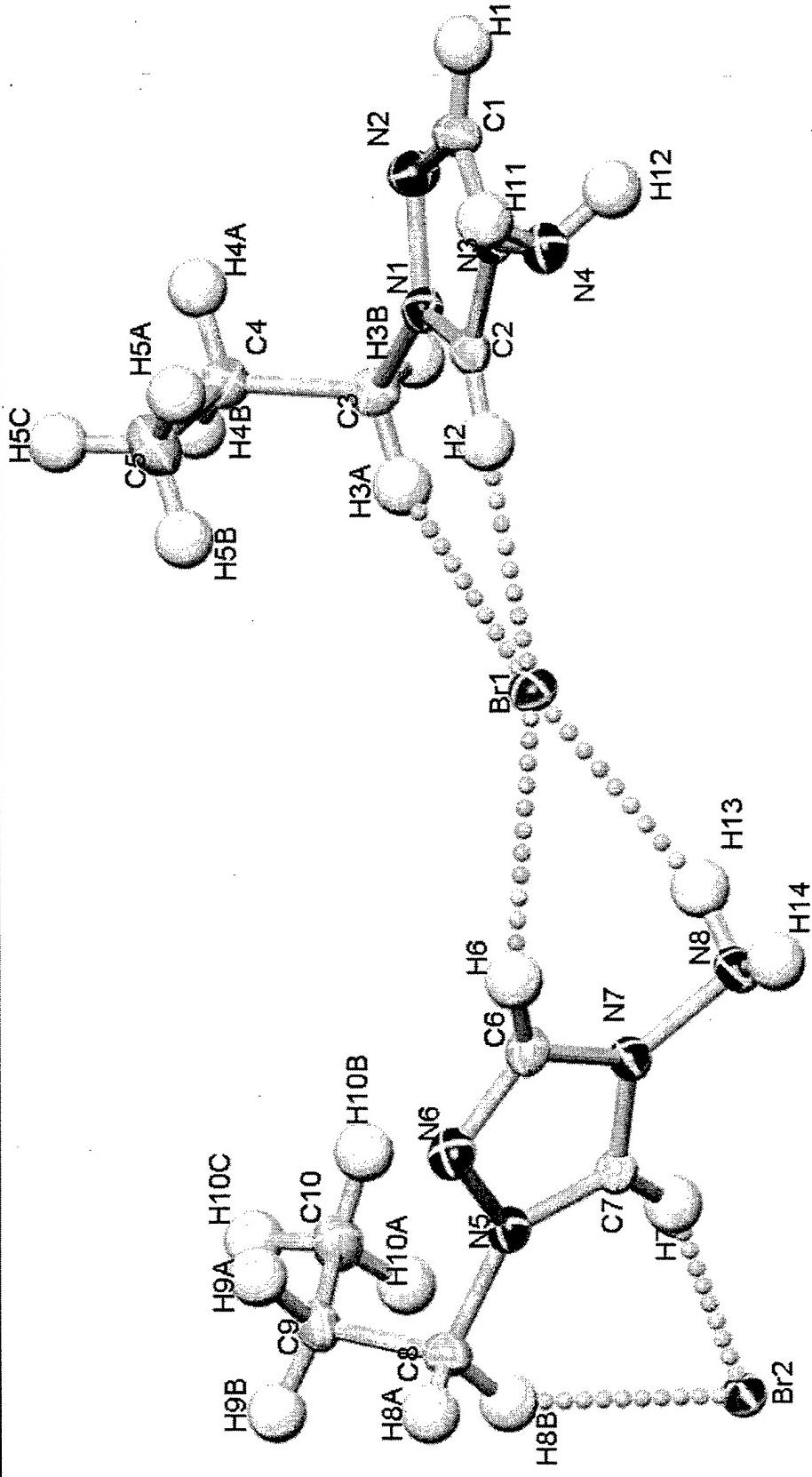
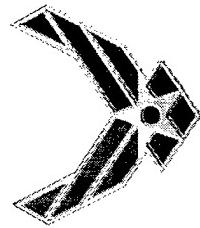
<sup>1</sup>H(left) and <sup>13</sup>C nmr spectra of 1-butyl-4-amino-1,2,4-triazolium bromide.

# Ionic Liquids

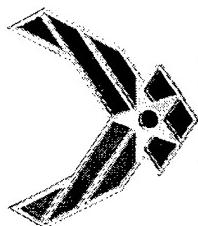


Single x-ray diffraction study of 1-ethyl-4-amino-1,2,4-triazolium bromide.

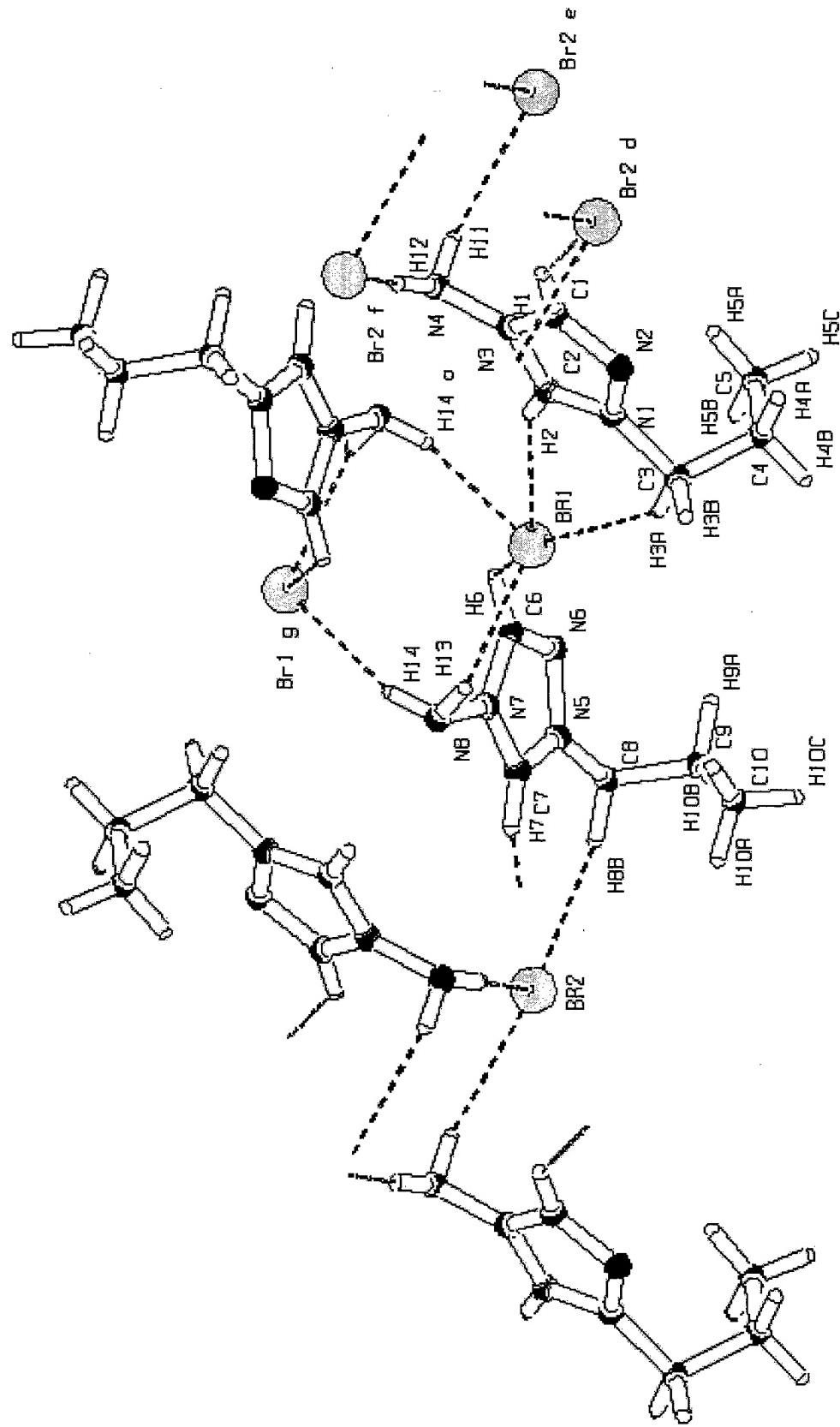
# Ionic Liquids



Single crystal x-ray diffraction study of 1-n-propyl-4-amino-1,2,4-triazolium bromide showing significant hydrogen bond contacts.

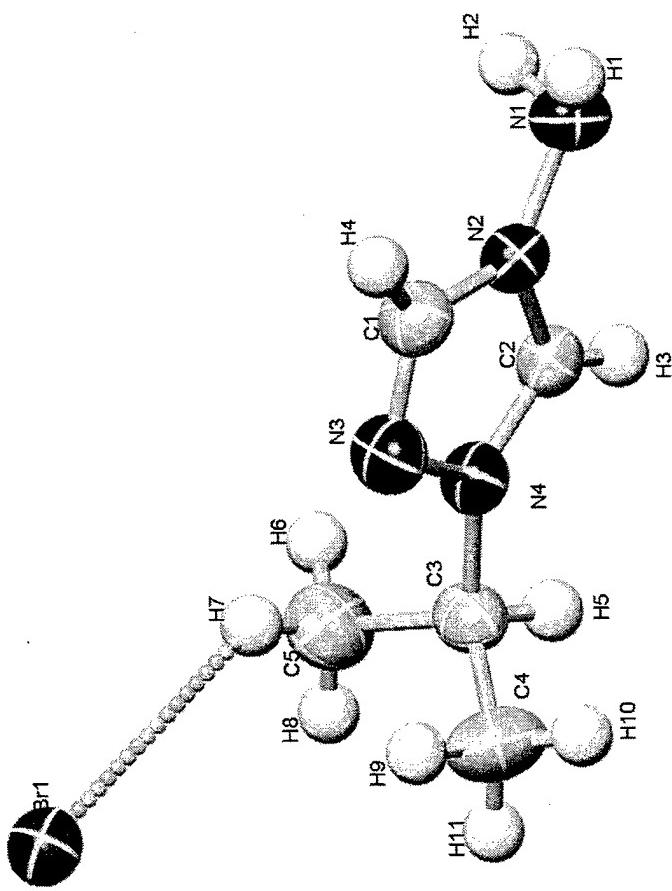


## Ionic Liquids



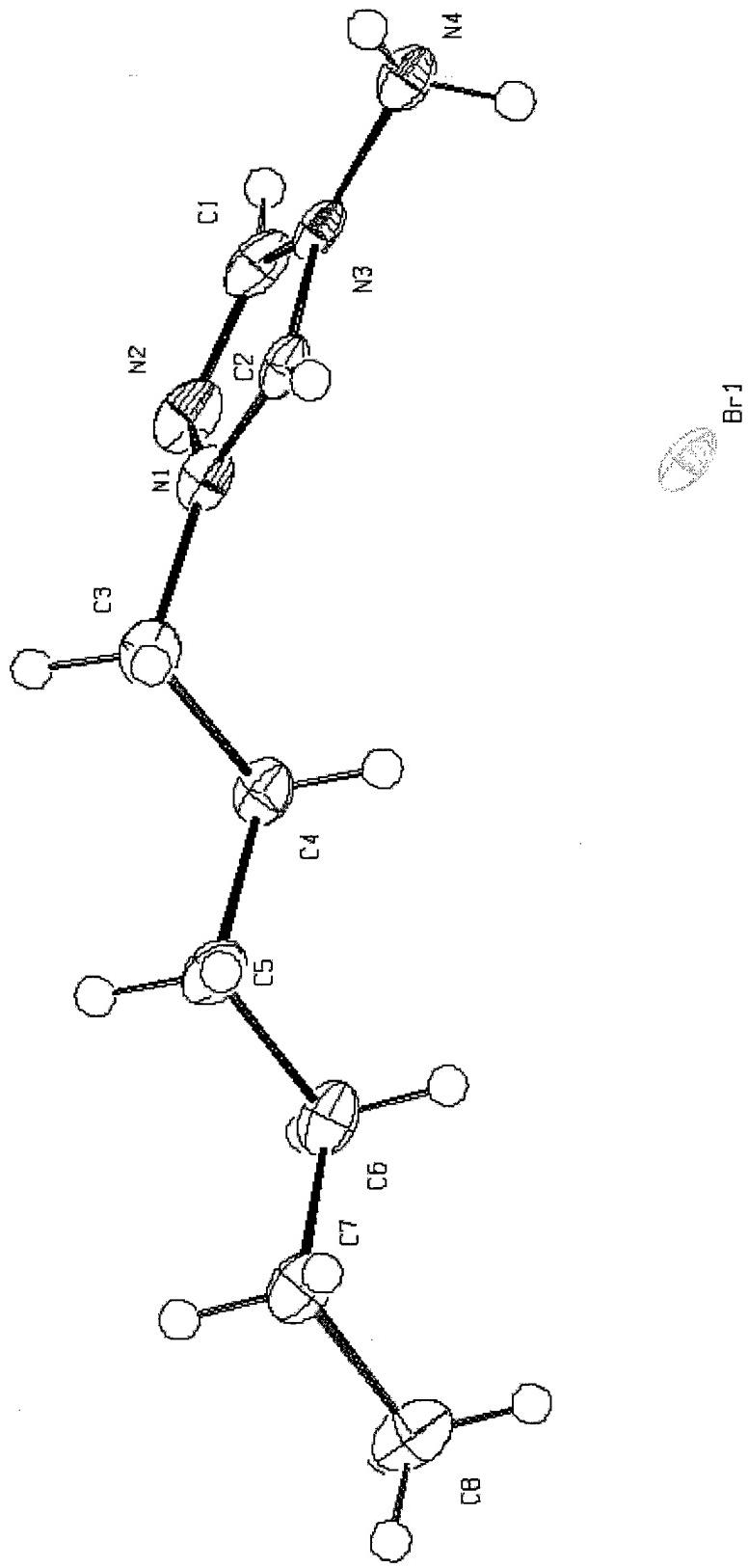
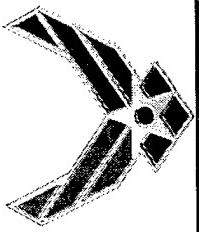
## Hydrogen bond contacts in solid 1-n-propyl-4-amino-1,2,4-triazolium bromide

# Ionic Liquids



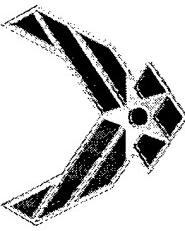
Single crystal x-ray diffraction structure of 1-isopropyl-4-amino-1,2,4-triazolium bromide.

# Ionic Liquids

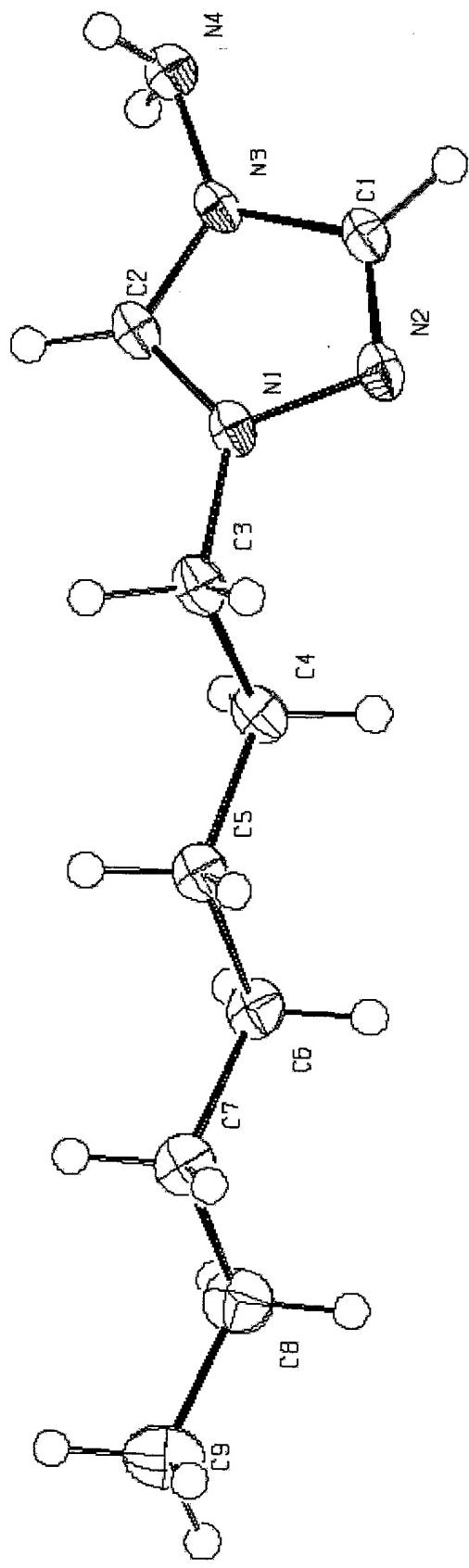


Single crystal x-ray diffraction study of 1-hexyl-4-amino-1,2,4-triazolium bromide.

# Ionic Liquids

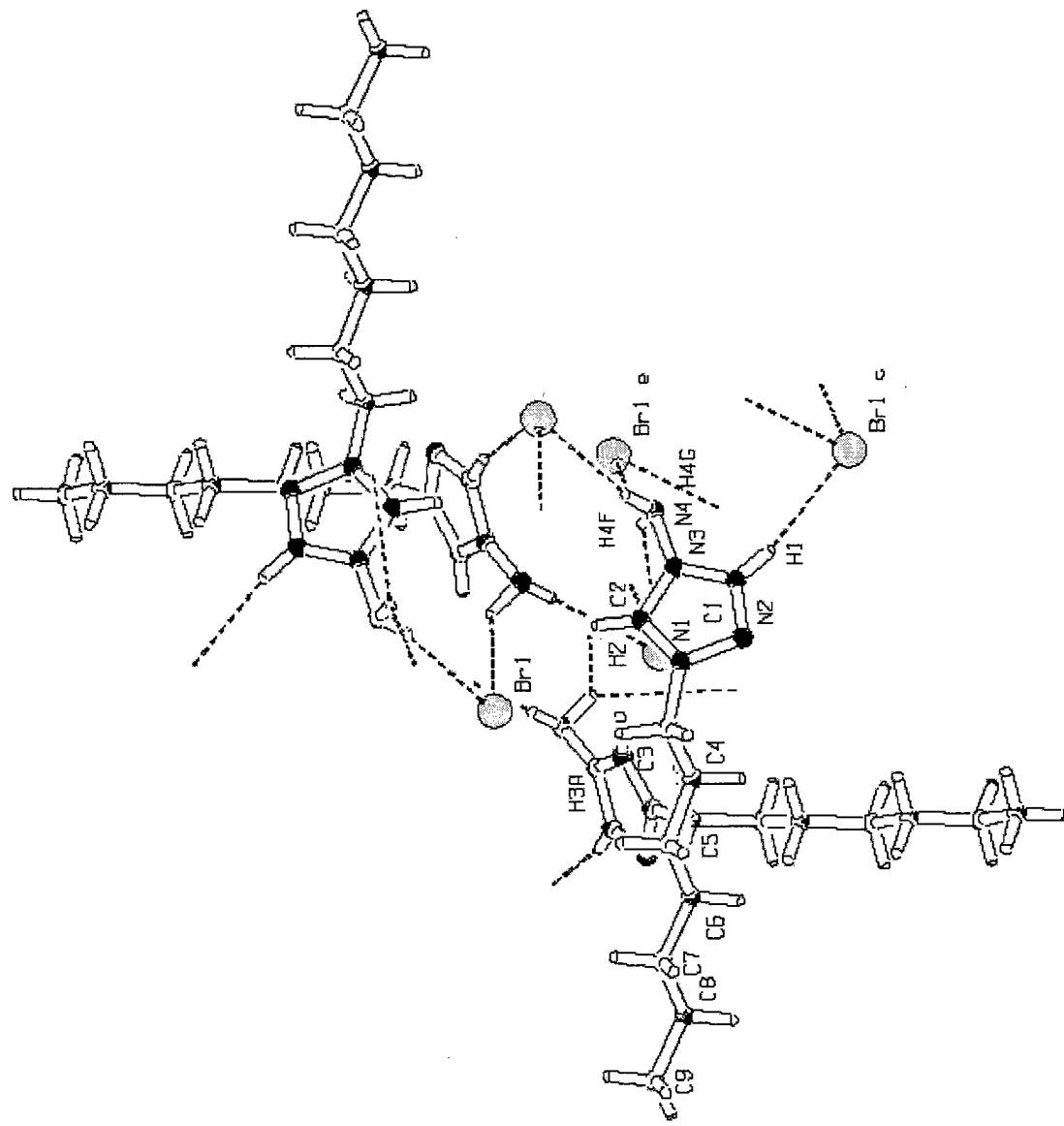
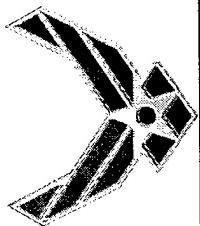


Br<sup>-</sup>



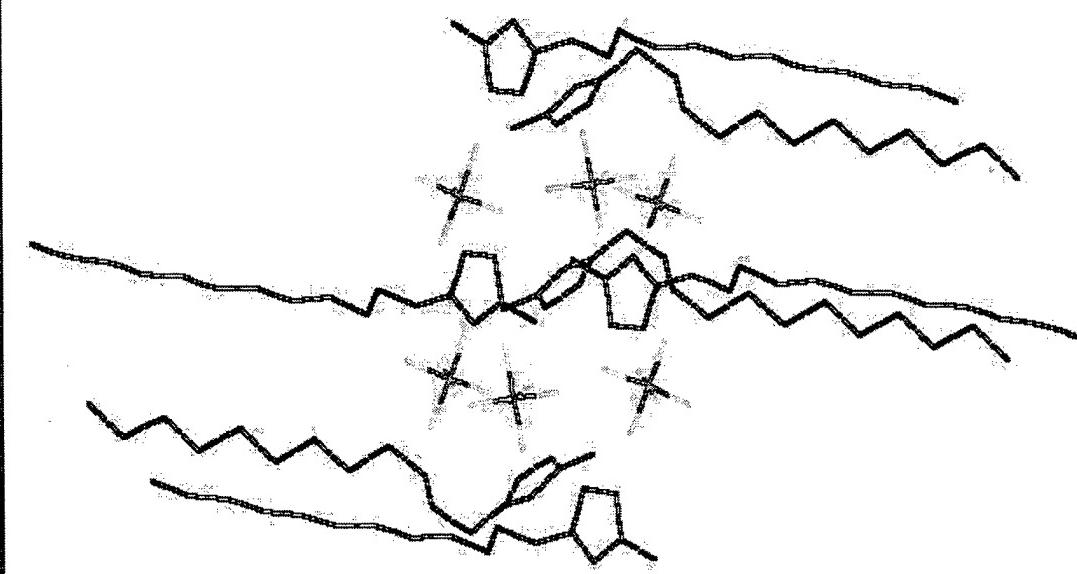
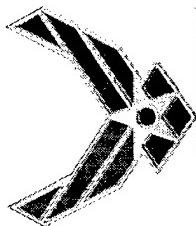
Single crystal x-ray diffraction study of 1-heptyl-4-amino-1,2,4-triazolium bromide.

# Ionic Liquids



Hydrogen bond contacts in 1-heptyl-4-amino-1,2,4-triazolium bromide

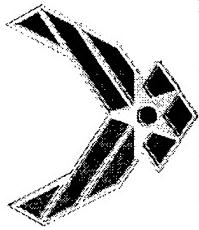
# Ionic Liquids



**1-dodecyl-3-methylimidazolium hexafluorophosphate\***      **1-hexyl-4-amino-1,2,4-triazolium bromide<sup>#</sup>**

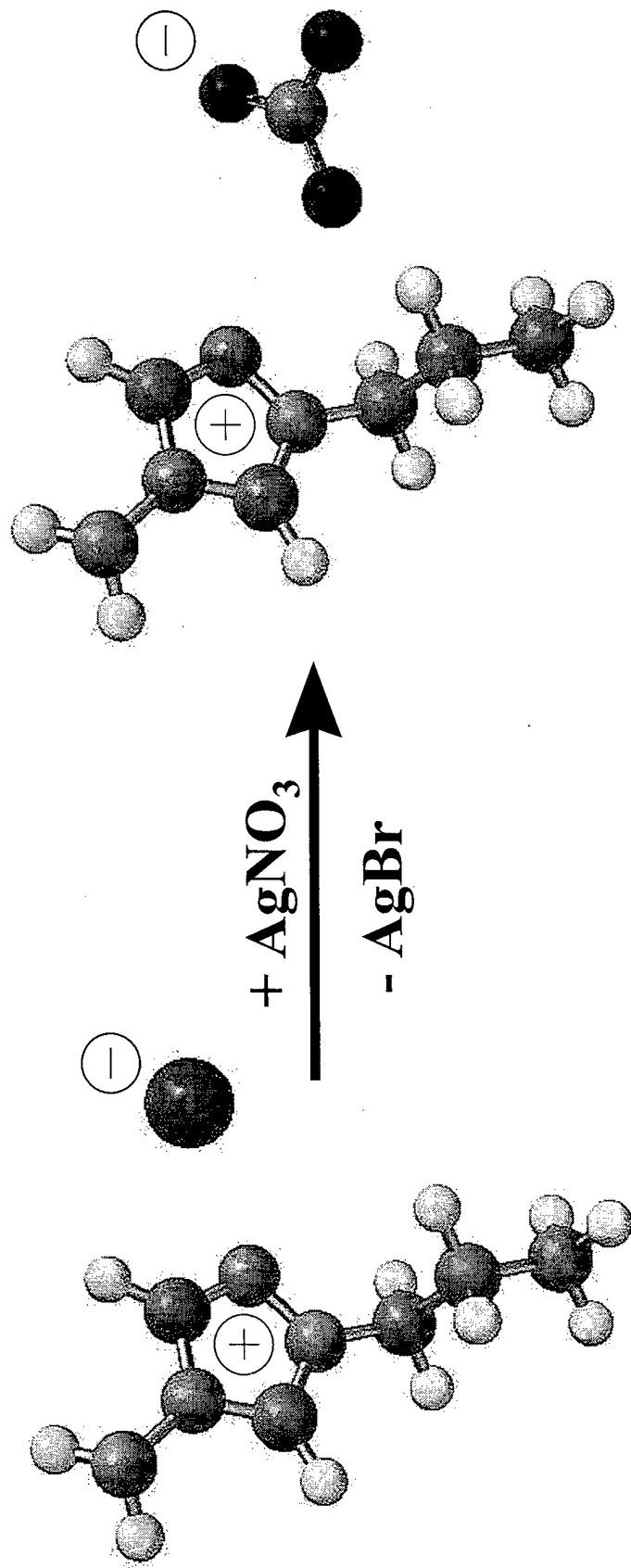
\*Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. *J. Mater. Chem.* **1998**, *8*, 2627. <sup>#</sup>Drake, G. W.; Tollison, K.; Hall, L.; Vij, A. 2003 manuscript in progress.

# Ionic Liquids



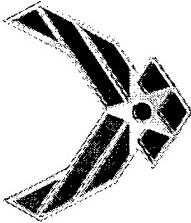
But halides are only the start...

Nitrates were best made through silver nitrate metathesis in methanol.



This route led to the best materials as the silver bromide was easily removed.

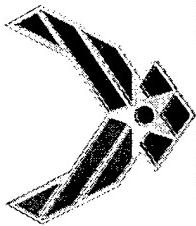
# Ionic Liquids



1-substituted-4-amino-1,2,4-triazolium nitrate salts are more stable.

<u>Salt</u>	<u>melting point(°C)</u>	<u>decomp onset(°C)</u>	<u>ρ(g/cm³, est.)</u>
1-methyl	54	185	1.57
1-ethyl	5	185	1.39 (1.38)
1-n-propyl	34	190	1.35
1-isopropyl	53	175	1.37 (1.43)
1-n-buty	-25 (g)	190	1.31
1-(2-ethanol)	-50 (g)	180	1.48
1-methylcyclopropyl	56	190	1.36 (1.44)
1-(2-propenyl)	10	165	1.23
1-n-pentyl	26	170	1.29
1-n-hexyl	-2	160	1.26
1-n-heptyl	31	160	1.24
1-n-octyl	29	170	1.22
1-n-nonyl	53	175	1.20
1-n-decyl	49	185	1.18

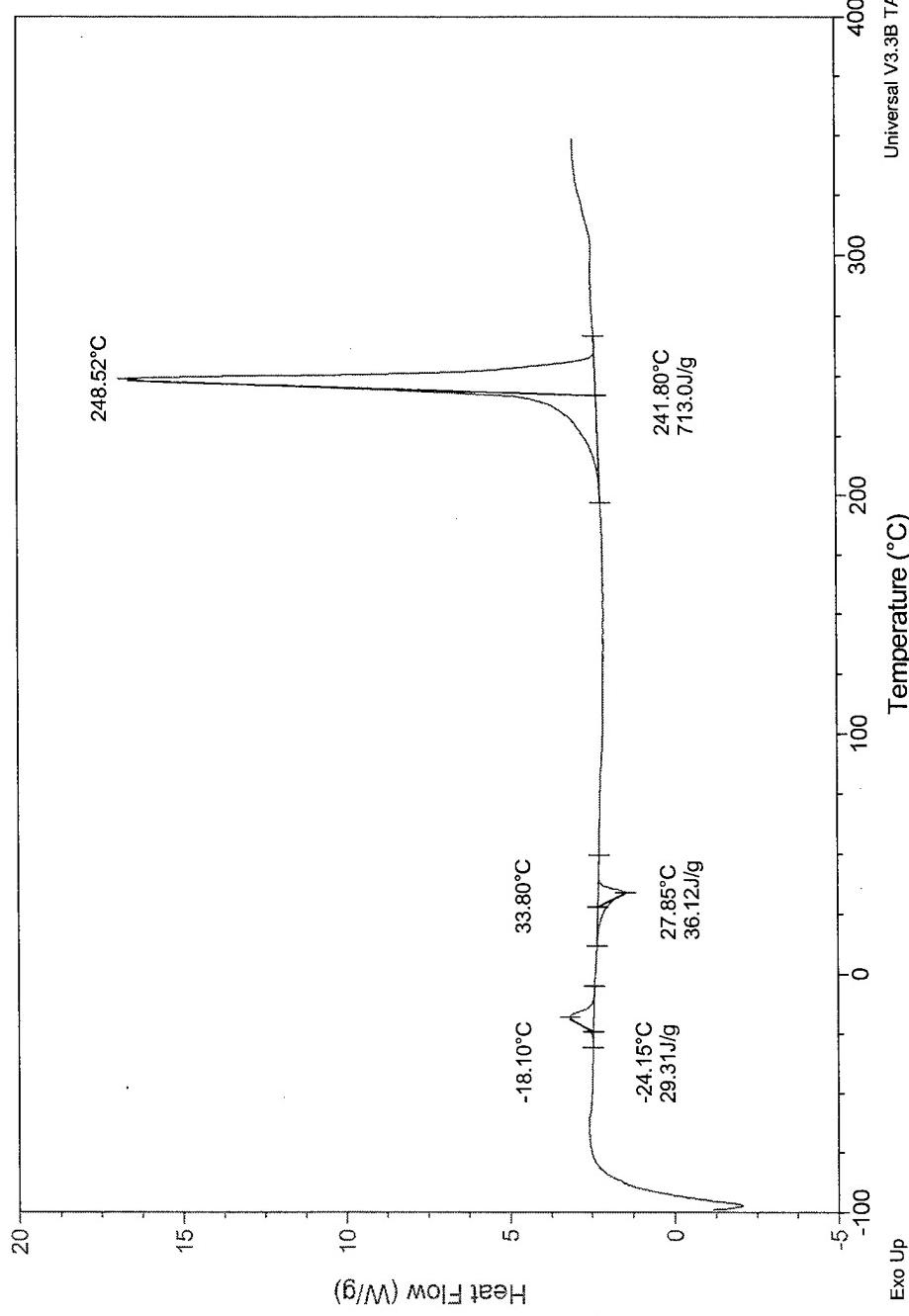
# Ionic Liquids



Sample: 1-PROPYL-4-AT NITRATE  
Size: 1.9000 mg  
Method: greg  
Comment: 10C/min/10ml/min/hermeticalpans

DSC

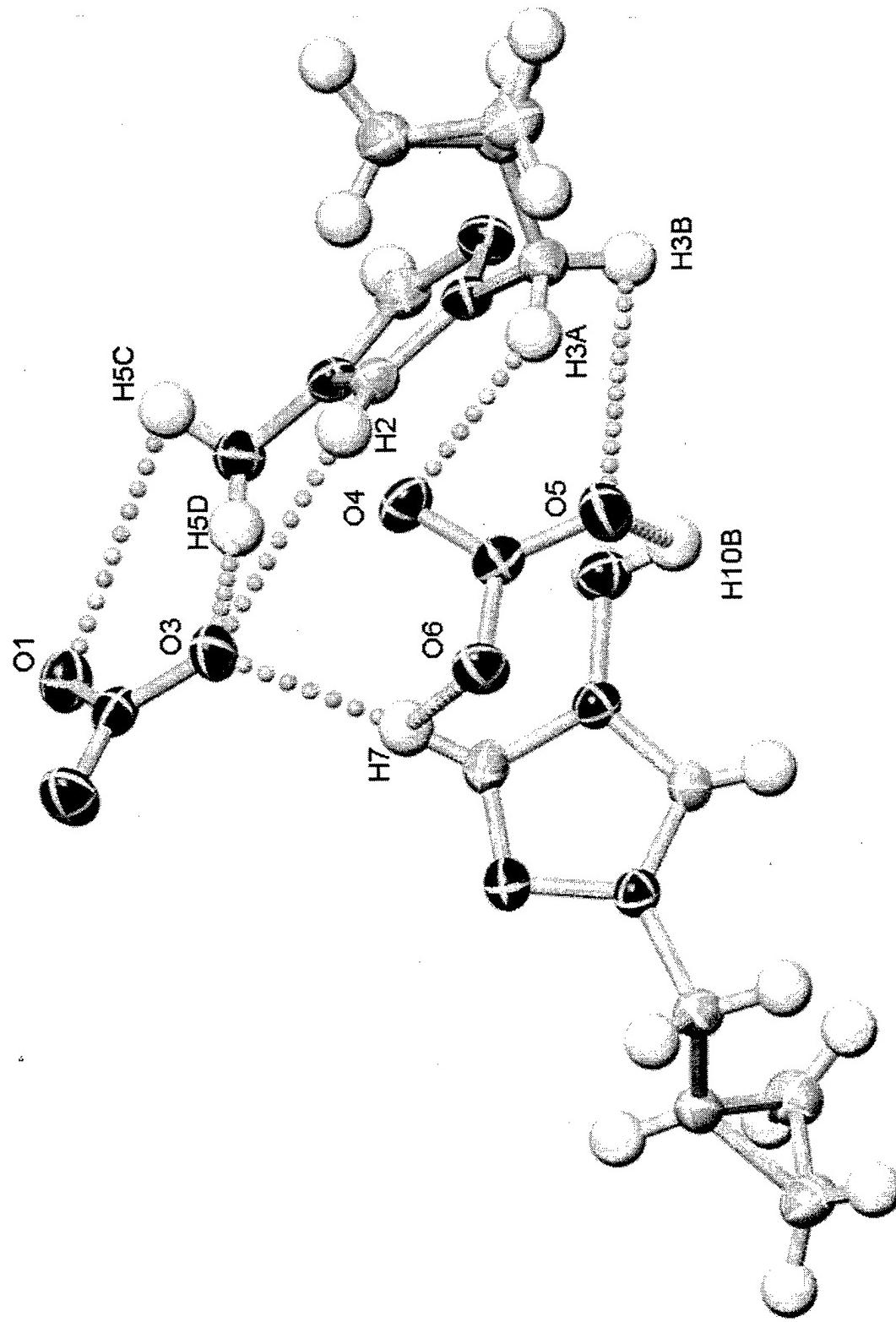
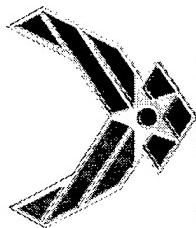
File: C:\...\files from old DSC\4at propyl no3  
Operator: DRAKE  
Run Date: 16-Jan-02 23:04



**DSC of 1-n-propyl-4-amino-1,2,4-triazolium nitrate**

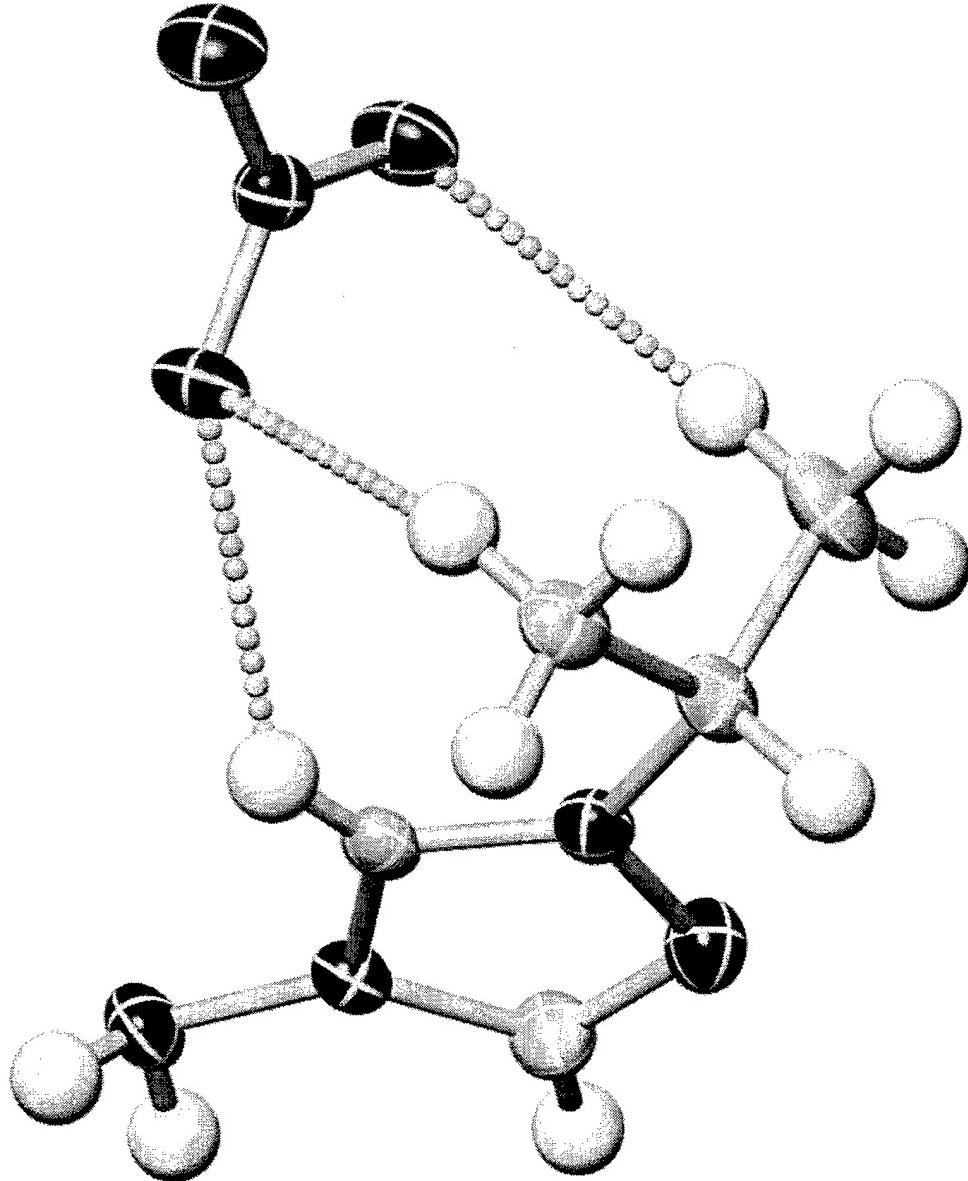
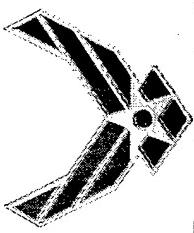
Universal V3.3B TA Instruments

# Ionic Liquids



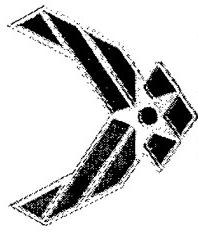
Single crystal x-ray diffraction study of 1-methyleclopolypropyl-4-amino-1,2,4-triazolium nitrate.

# Ionic Liquids

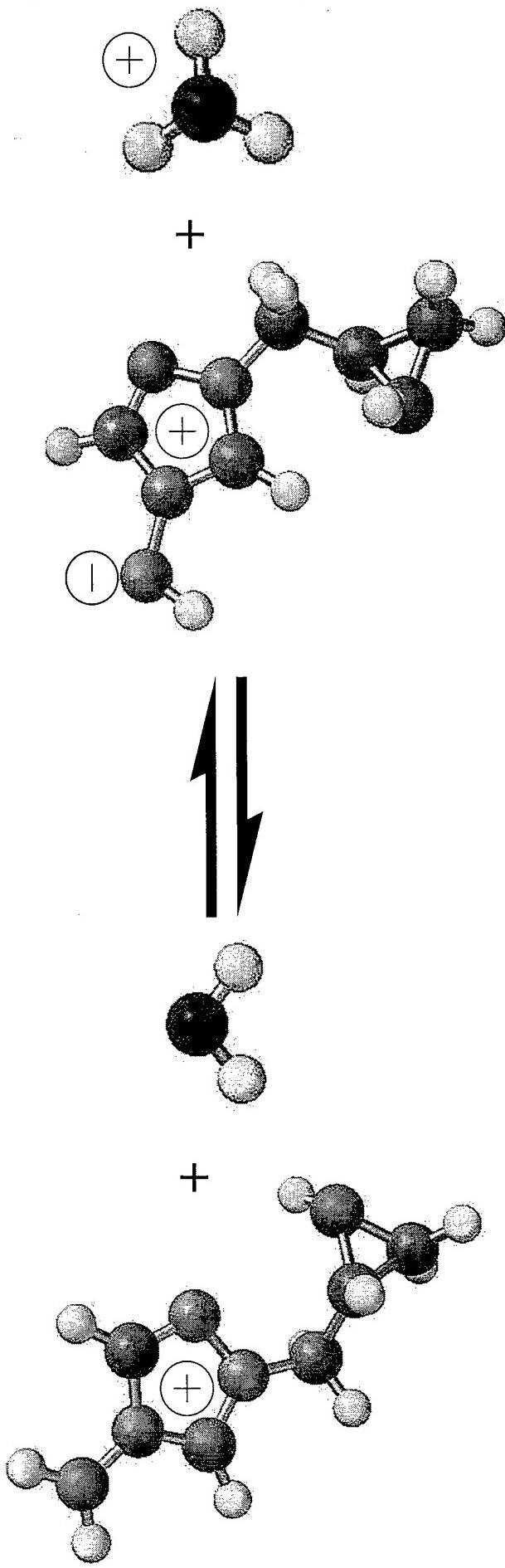


Single crystal x-ray diffraction structure of 1-isopropyl-4-amino-1,2,4-triazolium nitrate

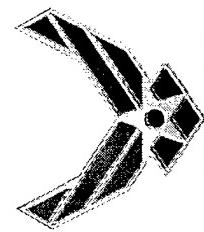
# Ionic Liquids



The new energetic cations are weakly acidic in nature, aqueous solutions have a pH of around 4 which suggests the equilibrium involving a zwitterionic 1-alkyl-4-amido-1,2,4-triazolium species. This equilibrium could be one possible way for the ionic liquids to “come apart”.



# Ionic Liquids



## Summary and Conclusions

Oxyamines and nitrocyanamide ions make for low melting and energetic salts, however both are plagued by poor thermal behavior and impact/friction sensitivity.

A large new class of low melting salts which should be considered as new members of the well known class of materials referred to as ionic liquids has been synthesized and well characterized.

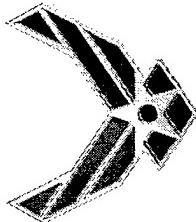
Using asymmetric cation shapes and poor cation-anion fit, an analogue system to the well known 1,3-dialkylsubstituted imidazolium cation family, based upon 1-substituted-4-amino-1,2,4-triazolium cations paired with the bromide and nitrate ions has been explored.

Facile synthesis routes from commercially available materials coupled with high yield and purity reactions make these new materials very exciting.

Several single crystal x-ray diffraction studies of several structures have been carried out proving the expected structure as well as revealing extensive hydrogen bonding in the solid state.

Physical properties of 1-substituted-4-amino-1,2,4-triazolium salts included much higher viscosities, higher densities, and much more polar behavior than that of imidazolium ionic liquids.

# Ionic Liquids



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